AN INVESTIGATION INTO SOME ASPECTS OF TRANSPORT PROPERTIES IN MOLTEN SALTS

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SUMMARY

This thesis embodies the results of an investigation of some aspects of transport phenomena in molten salts.

The subject of molten salts and their relevance to the theory of the liquid state is discussed, together with a brief survey of the experimental results which have been gained concerning these liquids.

The concept of transport numbers in molten salts has been investigated both experimentally and theoretically. Experiments are described in which transport numbers in a pure molten salt (lead chloride) have been measured.

An investigation of concentration cells with transference, containing molten salt electrolytes, has been carried out and the results of the investigation are presented herein. The results obtained are expressed by values of the electromotive forces of the cells, measured as a function of the temperature and composition of the molten salt electrolytes. Further, values for the diffusion potential, pertaining to liquid junctions between molten salt mixtures of varying nature and composition, have been deduced.

The E.M.F. and diffusion potential data has been interpreted in respect of the microscopic structures of the molten electrolytes, and a theoretical discussion of the E.M.F. of the cells, and of the diffusion potential, is also presented. The theoretical calculation of diffusion potentials is discussed in detail.

CHAPTER 1

GENERAL INTRODUCTION

1. Preliminary

Apart from the numerous technological applications of molten salts, in such fields as extraction metallurgy, nuclear reactors, fuel cells and thermocells, etc., they are of considerable theoretical interest. As a class of liquids - albeit liquids which exist only at relatively high temperatures - molten salts provide an avenue of approach to the general problem of the structure of liquids. Those properties of liquids, which relate to the motion of the constituent "particles", are readily susceptible to quantitative measurement in molten salts. The ionic character of molten salts allows measurement of such properties as electric conductance, transport number, and electrochemical properties pertaining to galvanic cells, etc. The information derived from such measurements can be of considerable value in treatment of the structure of liquids.

2. The Liquid State

There are general difficulties involved in exact mathematical interpretation of the liquid state. On the one hand, the structure is more diffuse than that of solids, so that it is not possible to make appeal to the structural regularity of solids, in which atomic motions may be regarded as a superposition of the normal modes of vibration for the lattice. Liquids, not too far from their melting points are, however, recognised as possessing a fairly high degree of short-range order, i.e. local "structure", similar in many respects to the short-range order of the solid formed on freezing, but they lack the long-range order of the solid. On the other hand, liquids cannot be treated from the same viewpoint as are (dilute) gases in which collisional encounters are rare and occur predominantly between isolated molecular pairs, although the essentially disordered nature of liquids, over macroscopic distances, is a property common to both liquids and gases.

Dynamically, any macroscopic system of molecules represents an N-body interaction problem, where N is a very large number. For the gas, a good starting approximation is to ignore interactions between molecules, thus reducing the problem to one involving N independent (non-interacting) bodies. In the solid, interactions between particles are large, but a simple co-ordinate transformation exists which, for small displacements, removes the interaction and again reduces the starting problem to one of independent bodies. No such general transformation has been found for the liquid, and the dynamical problem remains essentially one of many, mutually interacting bodies.

Since even the problem of three bodies interacting with inverse square forces has never yielded a complete solution, the intractability of the liquid problem can be readily appreciated. This state of affairs has led, on the one hand to the invention of a number of simplified models which are susceptible to mathematical analysis and, on the other hand, to the recasting of basic relations in many abstruse forms into which fruitful mathematical approximations can be inserted. No simple approach has gained dominance, and all approaches together fail to provide thoroughly accurate predictions, from first principles, of the major observable features of even simple liquids. Nevertheless, a fairly satisfactory understanding of some of these features is possible, in spite of the lack of precision, elegance and completeness of the theories.

Theories of the liquid state have developed from considerations of the two extremes of the liquid range - the solid state and the gaseous state - notwithstanding the inherent limited applicability to liquids, of concepts pertaining to the other two states of matter. Early theories of liquids were thus based on the hypothesis that liquids can be regarded as compressed gases. Such theories have also been proposed quite recently (see for example, Green [1] and McCall et.al. [2]). Parallel to the development of "compressed-gas" theories of the liquid state has been the development of theories based on the hypothesis that liquids can be treated as disordered solids.

1. Green, "The Molecular Theory of Fluids", North-Holland, Amsterdam (1952)
2. McCall, Douglass and Anderson, Phys.Fluids, 2, 87 (1959)

This hypothesis has arisen largely as a result of the X-ray diffraction evidence for short-range order in liquids [1]. The correct viewpoint obviously lies between the two extremes (solid and gas) and probably the major deciding factor is the temperature of the system. The existence of a liquid in equilibrium with its vapour is restricted to the relatively narrow region lying between its triple point and critical point. At the triple point, a liquid demonstrably retains many of the characteristics of a solid, while acquiring to some extent the characteristics of a gas. The former are not completely lost nor the latter fully developed until the critical point is reached. Above the critical point, according to the theory of the continuity of states [2], the liquid and its vapour are indistinguishable, while immediately above the freezing point it is highly probable that the liquid has much of the character of the solid from which it is derived.

Superimposed on these variations in emphasis has been the growth of attempts to deduce the structure of a liquid without recourse to the structure of the related solid or gas, by calculation of the distribution of particles which should arise, assuming a certain intermolecular force law [3].

The various general theories of the liquid state which have been proposed will not be discussed in detail here, since we are concerned rather with the application of the theories to molten salts. Suffice to indicate the

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1. Zernicke and Prins, Z. Physik, 41, 184 (1927)
2. Andrews, Phil. Trans., 159, 575 (1869); 161, 241 (1876)
3. Reiss, Frisch and Lebowitz, J.Chem.Phys., 31 , 369 (1959)

types of approaches which have been used: Quasi-lattice model[1,2], hole model [3, 4], cybotactic model [5, 6], polyhedral hole model [7, 8], liquid free-volume model [9-12] and significant-structure model [13-15]. Recently a detailed comparison of the various theories of liquids with the significant-structure theory, has been presented by Ree, Ree and Eyring [16].

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1. Frenkel, Acta Physicochim. URSS, 3, 633, 913 (1935)
2. Bresler, Acta Physicochim. URSS, 10, 491 (1939)
3. Altar, J.Chem.Phys., 5, 577 (1937)
4. Furth, Proc.Camb.Phil.Soc., 37, 252, 276, 281 (1941)
5. Stewart, Phys.Rev., 37, 9 (1931)
6. Mott and Gurney, "Electronic Processes in Ionic Crystals", Oxford, New York (1957)
7. Frank, Proc.Roy.Soc., (London), A215 43 (1952)
8. Bernal, Nature, 185, 68 (1960)
9. Eyring and Hirschfelder, J.Physic.Chem., 41, 249 (1937)
10. Kirkwood, J.Chem.Phys., 18, 380 (1950)
11. Cohen and Turnbull, J.Chem.Phys., 29, 1049 (1958); 31, 1164 (1959)
12. Turnbull, GE Res.Lab. Reprint 61-RL-2761 M
13. Eyring, Ree and Hirai, Proc.Natl.Acad.,Sci., 44, 683 (1958)
14. Carlson, Eyring and Ree, Proc.Natl.Acad.Sci., 46, 333 (1960)
15. Blomgren, Ann.N.Y.Acad.Sci., 79, 781 (1960)
16. Ree, Ree and Eyring, J.Physic.Chem., 68, 1163 (1964)

3. The Structure and Constitution of Molten Salts

Two of the most significant characteristics of molten salts, in relation to their constitution, are their fluidity and the fact that their constituent particles are electrically charged. An adequate theory of the liquid state must explain the ease of flow of molten salts, while at the same time taking account of the apparently contradictory fact that the packing densities are nearly equal to those of the corresponding solids. That the density change which takes place on melting must have a profound effect on the "molecular motion" is indicated by, for example, the fact that self-diffusion coefficients in molten salts are generally 100 to 1000 times greater than in the corresponding solid salts. The flow properties must reflect distinctive modes of "molecular" motion, the motion being basically a complicated Brownian movement.

The fact that the electrostatic binding energy in an ionic assembly (i.e. compared to a covalent assembly) has primary significance for fused salts is clear from the very high melting and boiling points, as well as the large magnitudes of the surface tensions at elevated temperatures. Clearly, the theoretical analysis of molten salts must take account of the Couloumbic interactions between the particles, and elucidate the role which these interactions play in ionic movements, etc.

Apart from simple ions, other entities which are in principle important in molten salts are holes (i.e. free-volume), ion-pairs or ion-associated groups, cationic and anionic complex ions, and molecules.

The presence of ions and holes is well established [1] by considerations of physical behaviour, but there is (and has been) considerable speculation regarding the existence of complex ions and molecules. There is, however, an almost continuous range of substances from those whose melts are virtually entirely ionic (e.g. NaCl [2]) to those for which there is good evidence that their melts contain primarily covalently bound molecules (e.g. the mercuric halides [3]) or complex ions. At the two extremes the relevant species present are readily distinguishable and may, with virtually no ambiguity be regarded as the fundamental units of which these melts are composed. For precision, in a statistical mechanical theory of molten salts containing only complex species, it would be necessary to include for each particle a set of internal co-ordinates describing rotational and vibrational degrees of freedom. The greatest conceptual difficulty in a statistical mechanical treatment of molten salts arises in those cases in which only partial association takes place fo form complex species (e.g. $CdCl_2$ [4]), or where association takes place to such a degree that large polymeric species are present (e.g. $ZnCl_2$ [5]).

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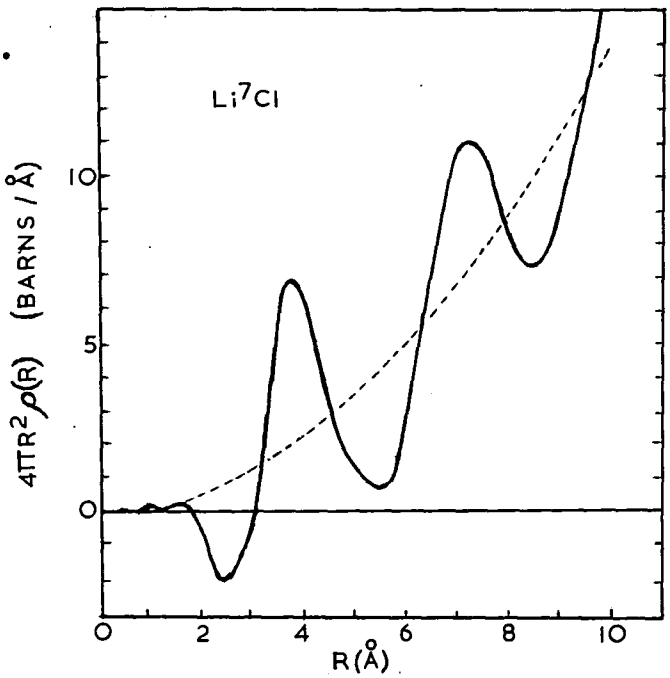
1. Bockris and Richards, Proc.Roy.Soc. (London), A241, 44 (1957)
2. Bockris, Crook, Bloom and Richards, Proc.Roy.Soc. (London), A255, 558 (1961)
3. Bues, Z.anorg.allgem.Chem., 279, 104 (1955)
4. Bues, Z.anorg.allgem.Chem., 279, 104 (1955)
5. Zarzycki, J.Phys.Radium, 19, 13A (1958) ; 18, 65A (1957)

Some of the most important evidence relating to the arrangement of ions in molten salts has been obtained by the detailed examination of X-ray and neutron diffraction patterns of these liquids. This work has been carried out on the liquid salts LiF [1], LiCl [1-3], LiBr [3], LiI [4], NaF [1-5], NaCl [1], NaI [3], KF [1], KCl [1-3], RbCl [6], CsCl [3], CsBr [3], CsI [3], CaF_2 [1] and $BaCl_2$ [1]. The results obtained for the alkali halides and the interpretation of these results have been discussed by Levy and Danford [7]. The most informative data is deduced from curves representing the radial distribution function (RDF) plotted against interatomic distance (r) (see Figure 1 below).



1. Zarzycki, J.Phys.Radium, 19, 13A (1958); 18, 65A (1957)
2. Lark-Horowitz and Miller, Phys.Rev., 51, 61 (1937)
3. Levy, Agron, Bredig and Danford, Ann.N.Y.Acad.Sci., 79, 762 (1960).
4. Zarzycki, Disc.Faraday Soc., 32, 38 (1961)
5. Zarzycki, Compt.Rend., 244, 758 (1957)
6. Levy and Danford, unpublished results.
7. Levy and Danford, in "Molten Salt Chemistry", editor Blander, 2nd chapter, Wiley, U.S.A. (1964)

The RDF curves obtained by X-ray diffraction have almost zero gradient and the RDF is close to zero, for small values of r.

This feature is said to be a consequence of the minimum distance of closest approach for atoms. An important feature of a typical curve is that at larger interatomic distances there is a series of broad, incompletely resolved peaks (whose widths are of the same order as atomic dimensions), which are ascribed to separations of atomic pairs at preferred distances. The positions, areas and widths of these maxima furnish the principal specific information regarding possible structural models. At distances large in comparison to atomic dimensions, most of the curves tend toward damped low-amplitude oscillations about a parabola. Comparison of the RDF curves for LiCl, obtained by X-ray diffraction and by neutron diffraction of a sample containing the isotope Li^7 (whose nuclear scattering amplitude is negative), yields striking evidence of charge ordering in the salt. The two curves are very similar, except that the first peak in the neutron diffraction RDF curve, corresponding to r = 3Å approximately, is negative, whereas the corresponding peak on the X-ray diffraction RDF curve is positive. This peak must therefore arise from interaction between dissimilar species (because only Li^7 - Cl interactions can give rise to a negative peak, Li^7 having negative nuclear scattering amplitude), implying that nearest neighbours in molten LiCl possess unlike charges. Furthe r, the persistent and marked fluctuations in the RDF curve from neutron diffraction, extending to interatomic distances of greater than 10 Å, indicates a tendency to charge alternation in successive

shells of neighbours about a given ion. The interpretation which has been suggested to account for this behaviour is that unlike species (presumably ions, Li^+ and Cl^-) predominate at interatomic separations of about 3, 6 and 9 Å, while like species predominate at about 4.5 and 7.5Å.

Detailed information concerning the number (i.e. co-ordination number) and separations of nearest neighbours has been deduced from examination of the first two peaks of the RDF curves. It appears, from this data, that for the alkali halides there is a uniform reduction in average co-ordination number on melting, from 6 for the solids to between 3.5 and 5.6 for the liquids. This reduction is accompanied by a decrease in the most frequent nearest neighbour separations, so that anion-cation distances are shorter than in the corresponding solids, by about 0.15Å.

Levy and Danford (1) have summarised the structural deductions from diffraction studies as follows: "...present knowledge of the structure of alkali halide melts as derived from diffraction measurements indicates a non-homogeneous microscopic environment in which first-neighbour cations form, on the average, a collapsed array (compared to the solid) about anions, and vice versa; second neighbours, tending to be of like charge, form, on the average, an expanded array compared with the solid. Charge-ordering to several atomic diameters is suggested, especially when the cation-anion radius ratio is small. However, the available information is not sufficient... to permit a detailed model to be formulated."

The properties of ion-pair distribution functions have recently been

1. Levy and Danford, in "Molten Salt Chemistry", editor Blander, 2nd chapter, Wiley, U.S.A. (1964)

investigated theoretically [1] for a simple molten salt model. The short-range ion-ion forces were assumed to be identical for both cations and anions and, although the method is capable of treating mixtures of ions with different charges, only a single fused salt of symmetrical valence type was considered. A set of relationships was developed to describe the asymptotic behaviour (for large interionic distances) of the ion-pair distribution functions. These relationships were obtained by invoking only certain weak, plausible assumptions, which circumvent the usual superposition approximation of liquid theory. A significant feature of the results is a prediction of concentric shells of average charge density, surrounding a given ion in a manner suggesting local lattice type structure.

(a) Structural Models

Structural models for pure ionic liquids have been discussed by Bockris et.al.[2-6] Many of the physical properties of molten salts have approximately the same magnitude as those of other liquids, e.g. surface tension viscosity, density, refractive index, self-diffusion co-efficients, etc. In contrast, however, some physical properties have very different magnitude to those of other liquids, e.g. melting point and boiling point and electric

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1. Stillinger, Kirkwood and Wojtowicz, J.Chem.Phys., 32, 1837 (1960)
2. Bockris and Lowe, Proc.Roy.Soc.(London), A226, 423 (1954)
3. Bockris, Mackenzie and Kitchener, Trans.Faraday Soc., 51, 1734 (1955)
4. Bockris, Tomlinson and White, Trans.Faraday Soc., 52, 299 (1956)
5. Bockris and Richards, Proc.Roy.Soc. (London), A241, 44 (1957)
6. Bockris, Crook, Bloom and Richards, Proc.Roy.Soc. (London), A255, (1960)

conductance.

Molten salts are known to be ionic conductors, and the main difference between the structures of ionic liquids and molecular liquids (such as benzene, for example) is that in the former a fairly high degree of short-range order is manifest by the arrangement of charged particles in (alternately charged) shells of nearest neighbours, whereas in the latter, such charge ordering does not exist.

The quasi-lattice, or vacancy, model [1-2] is based on the concept of a liquid as a disordered solid. In effect, the solid lattice is presumed to persist to a reasonably large extent on melting, but is injected with lattice defects (predominantly Schottky defects) of such a number as to produce the observed volume change on melting. Short-range order is preserved, in principle, but long-range order is destroyed, thus satisfying one of the requirements of experimental data for molten salts (i.e. the observations of short-range, but not long-range structure, made by X-ray and neutron diffraction studies). In respect of prediction of the magnitude of physical properties of molten salts, this model is only partially satisfactory.

The hole model [3-4] in application to molten salts is a significant advance on the quasi-lattice model. The hypothesis of a quasi-lattice is not employed and the volume increase on fusion is regarded as not being due to Schottky defects (vacant lattice sites, in effect), but rather to the introduction

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1. Frenkel, Acta Physicochim. URSS, 3, 633, 913 (1935)
2. Bresler, Acta Physicbchim. URSS, 10, 491 (1939)
3. Altar, J.Chem.Phys., 5, 577 (1937)
4. Furth, Proc.Camb.Phil.Soc., 37, 252, 276, 281 (1941)

of randomnly distributed holes, which arise from density fluctuations. On the basis of this model, the volume changes and entropy changes on fusion of salts may be calculated with reasonable accuracy, while the isothermal compressibilities and isothermal expansivities are calculable to a very good approximation.

The cybotactic, or crystallite model [1-2] arises from the concept of microdefects in solids. Macrodefects (i.e. dislocations) may be regarded as the source of an essentially similar model for liquids. Near the melting point, lattice defects are considered to diffuse to the dislocation lines of the crystal, leading finally to the formation of sheets of vacancies. The melting process involves the break up of the crystal along the sheets to form crystallites (or cybotactic groups) with fluctuating boundaries. The ability of this model to predict values of the physical properties of molten salts has not been examined.

The polyhedral-hole model [3-4] is related to the cybotactic model. It is based on the observation by Frank[3] that for a system of (spherical) particles of co-ordination number 12, the particles can be arranged in space in such a manner that each is at the centre of a face of a dodecahedron. For such an arrangement, the cohesive energy from short-range interactions is greater than for other possible arrangements, and the arrangement does not fill space completely; i.e. "holes" must be associated with the structure.

1. Stewart, Phys.Rev., 37, 9 (1931)
2. Mott and Gurney, "Electronic Processes in Ionic Crystals" Oxford, New York (1957)
3. Frank, Proc.Roy.Soc. (London), A215, 43 (1952)
4. Bernal, Nature, 185, 68 (1960)

Bernal [1] has concluded that, of a number of possible polyhedral arrangements, three have fivefold symmetry and do not pack together and, thus, form aggregate containing holes. This model involves the concepts of holes and crystallites as well as providing an explanation of the differences between liquids and the corresponding solids. The model has not been tested quantitatively to date, but it is noteworthy that the average co-ordination number of several alkali halides, as found by X-ray diffraction, is in the vicinity of 5, as predicted from Bernal's model.

The liquid free-volume model [2-5] is based on the concept of a liquid as a highly compressed gas, in which free volume is small compared to the space occupied by the particles. The "cell" in which a particle is "contained", has associated with it a certain free volume, which is equal to the difference between the total volume in which the particle can move, within a cell, and the volume of the particle itself. The theory has been subjected to various refinements, but overall it is not possible, using this model, to make accurate predictions of physical data.

The significant-structure model [6-8] assumes that the particles have differing degrees of freedom, within the same liquid. Fusion is presumed to occur by the creation of two distinct types of defects - holes and

1. Bernal, Nature, 185, 68 (1960)
2. Eyring and Hirschfelder, J.Physic.Chem., 41, 249 (1937)
3. Kirkwood, J.Chem.Phys., 18, 380 (1950)
4. Cohen and Turnbull, J.Chem.Phys., 29, 1049 (1958); 31, 1164 (1959)
5. Turnbull, GE Res.Lab. Reprint 61-RL-2761 M
6. Eyring, Ree and Hirai, Proc.Natl.Acad.Sci., 44, 683 (1958)
7. Carlson, Eyring and Ree, Proc.Natl.Acad.Sci., 46, 333 (1960)
8. Blomgren, Ann.N.Y.Acad.Sci., 79, 781 (1960)

dislocations. Some of the particles vibrate around equilibrium positions like the particles of a crystalline solid; others move like particles in the gaseous state. The partition function of the system is a product of contributions from both the solid-like and gas-like structures. The volume and entropy changes on fusion can be predicted fairly well from this model.

Overall, of the current theories, the hole model of liquids appears to give the best representation of molten salts.

(b) Mixtures of Molten Salts

The study of mixtures of molten salts is important in that it provides a means of testing models for pure salts, by comparison of the observed and predicted behaviour on mixing. Mixtures may be classified on the basis of their thermodynamic properties; thus, the criteria of thermodynamically ideal behaviour can be applied. In practice, most binary molten salt mixtures do not exhibit ideal behaviour, and the magnitude of deviations from ideal behaviour appears to offer a means of differentiation of salt mixtures into two broad groups - those whose deviations from ideal behaviour are (a) less than and (b) greater than, arbitrary values.

For the class of systems whose properties show small deviations from ideal values, the molar volume isotherms are linear to within about 0.2% and electric conductance isotherms deviate from ideality (additivity) by not more than, about 15%[1]. The conductance isotherms for such systems generally show no minima, molar refractivities are linear functions of com-

1. Bloom and Bockris, in "Fused Salts", editor Sundheim, Chapter 1, McGraw-Hill, U.S.A. (1964)

position, and thermodynamic activities and surface tensions deviate by not more than about 10%, in general, from the ideal solution values.

In such cases, then, the process of mixing appears not to be accompanied by marked structural changes. Strictly speaking, however, it is possible to infer only that the mixing process does not lead to changes, in the melt, of such nature and magnitude to markedly affect the above mentioned properties. There could be, in principle, marked structural changes which are not manifest in appreciable deviations from ideality in those properties considered above.

Many binary systems of liquid salts show large deviations from ideal behaviour, and such mixtures have been grouped, on that basis, in a second class of nonideal systems. An experimental criterion for this classification which has been applied is, for example, deviations of more than 15% from ideal values, of equivalent conductance isotherms. Minimum thermodynamic activity at particular compositions [1], deviations of molar refractivity from ideal values [2] and large negative deviations from ideal-mixture surface tension values [3] have been found for such mixtures.

The behaviour of this second class of binary systems has been interpreted as being due to the formation, on mixing, of complex ions. A natural extension of this interpretation, used to explain the pseudo-ideal behaviour of the first class of binary systems, is that in the latter complex

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1. Bloom and Richards, to be published; Richards, Ph.D. Thesis, University of New Zealand (1956)
2. Bloom and Peryer; to be published
3. Bloom, Rev.Pure Appl.Chem., 9, 139 (1959)

ions are either not formed or else their lifetime is so short that they do not appreciably change the values of the properties mentioned [1].

The validity of this interpretation, of deviation from their ideal values of various properties of molten salt mixtures, has been the subject of considerable discussion. There is a great deal of experimental data for which the postulate of the formation of complex ions is probably sufficient to explain the observed behaviour; whether this postulate is also necessary has not been effectively demonstrated. The question of complex ion formation is discussed in Chapters 3 and 4 of this thesis, and will not, therefore, be dealt with in detail here. It is important, however, to state at this juncture that all deviations in properties from their ideal values must be due to such changes in "structure" as are reflected in those properties in question and not necessarily in all properties of the salt(s). These structural changes are not necessarily due to the formation of complex ions on mixing, unless it can be demonstrated with certainty that there is no other possible source of the observed behaviour.

(c) The Concept of a Complex Ion in Molten Salts

There is obviously a wide range in the nature, degree and strength of interactions between the species constituting a molten salt. In molten sodium chloride the structural entities are presumed to be Na^+ and Cl^- ions, and it is theoretically unlikely that ion association, producing relatively strongly bound complex species, would take place in pure sodium chloride at least at temperatures well below the boiling point. It is possible that ion-pairs (Na^+Cl^-)

1. See, e.g. Bloom & Bockris, in "Fused Salts" editor Sundheim, Chap. 1, McGraw-Hill, U.S.A. (1964)

could be formed, by interpenetration of the electron clouds of Na^+ and Cl^- ions due to momentary close approach of the two ionic species. The average lifetime of such an entity is likely to be very short (because there is no strong chemical bond between the components), even though there may be a finite number of such ion-pairs in existence at a particular instant of time. At the other extreme, the bonding in a complex ion such as $CdCl_3^-$ (which is a well known species, in aqueous solution chemistry particularly) is probably very largely covalent, and the lifetime of such a species, in a molten salt, could therefore be relatively long. By the same token, it is reasonable to presume that a range of complex ions exist, in which the bonding varies between the extremes of virtually pure covalent character and virtually complete ionic character. The lifetimes of such complexes would vary then, according to the strength of the metal-ligand bonding.

Such species as (Na^+Cl^-) ion-pairs (whose bonding we will presume to be close to 100% ionic, at temperatures well below the boiling point) would contribute to diffusion, in a molten salt system, but not to electric conductance[1] because the components of this species would perform the same translational motion, when associated as (Na^+Cl^-). Bloom and Bockris[2] define a complex ion in relation to the motions of its constituents: "A complex ion is an entity in which the individual particles carry out identical translatory movements in diffusion". The ion-pair (Na^+Cl^-) is thus a complex ion

1. Borucka, Bockris & Kitchener, Proc.Roy.Soc.(London), A241, 554 (1957)
2. Bloom & Bockris, in "Fused Salts", editor Sundheim, Chapter 1, Wiley, U.S.A. (1964)

according to this definition. However, the lifetime of (Na^+Cl^-) species would be so short that such a species would not be detectable by conventional means: if one accepts the postulate that an entity can have existence only if its existence is detectable then the definition above must be modified. Thus, we might perhaps, define a complex ion as an entity all of the components of which carry out identical translational diffusive movements, and whose average lifetime is sufficiently long for the species to be detectable as a distinct entity. The actual magnitude of the lifetime necessary will depend, of course, on the detection technique used.

Proof of the existence of complex ions in a pure molten salt, or molten salt mixture, must inevitably depend on observations of behaviour which are consistent only with the presence of complex species in the salt. That is, it must be established beyond doubt that if complex ions were not present then the behaviour of the system would be different from the observed behaviour. It is not sufficient for the observed behaviour to be consistent with the formation of merely a <u>new</u> entity; it must be demonstrated conclusively that the new entity is in fact a complex ion and not, for example, a simple ion formed by dissociation of a complex species which is present in one of the (pure) component salts before mixing with the other.

4. Experimental Methods for the Elucidation of the Structure of Molten Salts

(1) Thermodynamic Activity

Activities in molten salt mixtures have been determined by a fairly wide variety of methods, both absolute and non-absolute. Methods which have been used include vapour pressure determination[1,2] (by several techniques), cryoscopy[3], equilibrium distribution of a solute between two immiscible phases[4] and measurements of the electromotive force of galvanic cells[5,6].

On the basis of deviations of activities from the values corresponding to ideal solution behaviour, various complex ionic species have been postulated for such binary systems as, for example, KCl - $PbCl_2$ and KCl - $CdCl_2$[7]. Complex ions which have been suggested are $CdCl_6^{4-}$ and $CdCl_4^{2-}$ (in KCl - $CdCl_2$ mixtures), and $PbCl_6^{4-}$ and $PbCl_4^{2-}$ (in KCl - $PbCl_2$ mixtures).

In some systems positive deviations of activities, from the ideal values, have been observed (e.g. NaCl - $PbCl_2$[8]). A possible interpretation of this behaviour is that pure lead chloride is itself associated to some extent (i.e. it contains "autocomplexes") and the addition of the highly polarising Na^+ ion to the salt causes dissociation into simpler species (e.g. $PbCl^+ \rightarrow Pb^{2+} + Cl^-$).

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1. Bloom & Welch, Trans.Faraday Soc., 57, 61 (1961)
2. Bloom & Welch, Disc.Faraday Soc., 32, 115 (1962)
3. Flood, Forland & Roald, J.Amer.Chem.Soc., 71, 572 (1949)
4. Heymann, Martin & Mulcahy, J.Physic.Chem., 47, 473 (1943)
5. Hildebrand & Salstrom, J.Amer.Chem.Soc., 54, 4257 (1932)
6. Lantratov & Alabyshev, Zh.Priklad Khim., 26, 263, 353 (1953)
7. Barton & Bloom, J.Physic.Chem., 63, 1785 (1959)
8. Bloom & Richards, to be published; Richards, Ph.D. Thesis, University of New Zealand (1956)

The detailed interpretation of activity data is not by any means unequivocal, because no precise relationship between activity and "structure" is known. In fact, in principle it is illogical to deduce the presence of complex ions, from deviations of activity from the ideal solution values, because the thermodynamic activity of a component in a mixture is defined quite independently of structural considerations. Thus, the measured activity of a component has in principlethe same value, independent of the nature of the species which are assumed to be present. The most useful information may be obtained by postulating the presence of certain species, assigning equilibrium constants to their formation reactions, calculating the form of the resulting activity isotherm and comparing with the experimental curve [1]. In this way it can be shown that the form of the experimentally determined activity isotherms can be theoretically reproduced within experimental error, suggesting that the original postulates are at least plausible.

(2) Surface Tension

For binary mixtures of molten salts, a quantitative treatment of surface tension, based on the propositions of Guggenheim[2], has been developed by Boardman et.al. [3] They showed that for an equimolar mixture of two components forming ideal solutions:

$$\gamma = \bar{\gamma} - (\Delta^2 a / 8kT) \qquad \ldots(1)$$

where $\bar{\gamma}$ is the arithmetic mean of the surface tensions of the components, Δ

1. Hildebrand & Scott, "Solubility of Non-electrolytes", Reinhold, New York (195
2. Guggenheim, "Mixtures", Oxford, New York (1952)
3. Boardman, Palmer & Heymann, Trans.Faraday Soc., 51, 277 (1955)

is the difference between these surface tensions and 'a' is the average area per molecule in the surface layer. When the two components have equal surface tensions, it follows from equation (1) that isotherms of surface tension against composition will be straight lines, the surface tension being constant over the whole composition range. In all cases where the surface tensions of the pure components are not equal, the isotherms will have negative deviations from ideality. Comparison of actual isotherms with the ideal values has been used to discuss the interactions in binary molten salt solutions [1].

Surface tension data have also been used in calculation of the energy of formation of holes in molten salts, from the equation

$$E_h = 4\pi r_h^2 \gamma \qquad \ldots(2)$$

where r_h is the radius of the mean hole. Such calculations have been of considerable value in the development of an equation of state for molten salts [2].

Bloom et.al. [3] have suggested that the surface heat of mixing may be used to discuss interactions in molten salt mixtures, because the formation of complex ions should lead to a decrease in surface heat of mixing, as well as a decrease in heat content on mixing in the bulk phase. The surface tension of a liquid is expressed by the relationship

$$\gamma = \frac{G^S}{a} \qquad \ldots(3)$$

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1. Boardman, Palmer & Heymann, Trans.Faraday Soc., 51, 277 (1955)
2. Bockris & Richards, Proc.Roy.Soc. (London), A241, 44 (1957)
3. Bloom, Davis & James, Trans. Faraday Soc., 56, 1179 (1960)

where a = area of surface per mole, G^S = free energy of surface per mole.

The surface entropy per unit area is given by

$$\frac{S^S}{a} = -\frac{d\gamma}{dT} \qquad \ldots(4)$$

and the surface heat content per unit area (total surface energy) is thus

$$\frac{H^S}{a} = -T\frac{d\gamma}{dT} \qquad \ldots(5)$$

For ideal mixtures the heat of mixing is zero, hence

$$\frac{\Delta H^S}{a} = \frac{H^S}{a} - \left[N_1 \left(\frac{H^S}{a}\right)_1 + N_2 \left(\frac{H^S}{a}\right)_2 \right] = 0 \qquad \ldots(6)$$

where $\frac{\Delta H^S}{a}$ is the surface heat of mixing per unit area, $\frac{H^S}{a}$ is the value for the mixture, and $\left(\frac{H^S}{a}\right)_1$ is the value for the component whose mole fraction is N_1 (similarly $\left(\frac{H^S}{a}\right)_2$, the value for the other component). Where complex ion formation takes place it would be expected that $\frac{H^S}{a}$ would be negative. This is the case for, for example, the system $PbCl_2$ - RbCl, in which the presence of complex ions has been fairly well demonstrated. Negative values for $\frac{H^S}{a}$ do not, of course, necessarily imply complex ion formation.

(3) Density

Measurements of the densities of molten salts and their mixtures provide little evidence in respect of the structure of the salts. If the nature of the structural groups present changes with temperature then such changes are reflected, with rather low sensitivity in the resulting changes in density. Klemm [1] has proposed that salt mixtures consisting of covalent

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1. Klemm, Z.anorg.Chem., 152, 295 (1926)

molecules, have larger molar volumes than have ionic salts, where coulombic forces are larger (than in covalent salts). This assertion is possibly true but it cannot be effectively tested by experiment.

For most mixtures of molten salts, the density isotherms show only very small (if any) deviation from additivity; i.e. the densities are close to the values given by the equation (for a two-component ideal mixture):

$$\rho = \rho_1 x_1 + \rho_2 x_2 \qquad \ldots(7)$$

where ρ_1 and ρ_2 are the densities of the pure components 1 and 2 and x_1 and x_2 are their mole fractions in the mixture. For the systems $CdCl_2$ - KCl and $PbCl_2$ - KCl marked positive deviations from additivity have been observed.[1]

(4) X-ray and Neutron Diffraction

The structural information which can be derived from such studies has been already discussed. To date, studies have been made only on pure salts; the extension of the techniques to molten salt mixtures is potentially a source of a great deal of direct evidence regarding the existence of complex ions.

(5) Molar Refractivity

Deviations from ideality in molar refractivity isotherms have been interpreted[2] as indicating the presence of complex ions in molten salt mixtures, but the structural information which may be gleaned from such data appears to be rather limited.

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1. Boardman, Dorman & Heymann, J.Phys. and Coll. Chem., 53, 375 (1949)
2. Bloom & Peryer, to be published.

(6) Heat Capacity and Thermal Data

Knowledge of heat capacities of molten salts is necessary to relate thermodynamic data of molten salts to those of the room temperature salts. The amount of structural information available from such data is small.

(7) Ultraviolet Spectra

Ultraviolet absorption spectrometry is of considerable value in investigation of complex ion formation in molten salts [1-3]. The basis of the method is comparison of the observed spectrum with that of an aqueous solution in which the nature of the complex entity is unambiguously known. Conclusions drawn from U.V. spectral data are not unequivocal because the data obtainable does not allow deduction of the structural entity from first principles without resort to a "standard." The fact that the "standard" used and the "unknown" are in quite different physical and chemical environments reduces the usefulness of the method. A combination of the results from various spectral methods may, however, yield valuable information.

(8) Raman Spectra

There have been no Raman spectral investigations, conducted on molten salts, which are capable of completely unequivocal interpretation. That is, conclusions have been drawn regarding structural entities, but

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1. Gruen, Nature, 178, 1181 (1956)
2. Gruen, J.Inorg.Nucl.Chem., 4, 74 (1957)
3. Sundheim & Harrington, J.Chem.Phys., 31, 700 (1959)

only be comparison of the data with data on the corresponding systems in different physical and chemical environment. For example, by comparison with the results obtained on aqueous solutions, the conclusion has been drawn that liquid $CdBr_2$ appears to be autocomplexed, as $CdBr_6^{4-}$ ions. The addition of KBr increases the intensity of a peak presumed to be due to $CdBr_4^{2-}$ ions, at the expense of the intensity of the $CdBr_6^{4-}$ ion peak. However, in the absence of sufficient data from aqueous solutions, the structural entities in molten salts cannot be established with any certainty from only the data pertaining to the salts.

In general, studies of Raman spectra of molten salts do offer a valuable method of elucidation of the structural entities present in the salts, in so far as such studies can lend support for or against particular postulates of the nature of species present.

5. Transport Properties of Molten Salts

The variety of transport processes which take place, and can be studied experimentally, in molten salts, offer particularly definitive methods of elucidation of the structures of these liquids.

(a) Theoretical Considerations

Transport phenomena are time-irreversible, steady-state processes, and, therefore, the "thermodynamics" of transport processes must be treated by the methods of non-equilibrium thermodynamics (and not by equilibrium thermodynamics, or "thermostatics").

Reviews of general theories of transport processes include those by Collins and Raffael [1], Green [2] and Rice and Frisch [3]. Kirkwood [4] has developed a general theory of transport phenomena, which is based on an extension of the concept of Brownian motion of molecules. A characteristic quantity which appears in this theory is a "friction coefficient", ζ . Kirkwood devised an explicit but intractable relationship between this "friction coefficient" and the various transport coefficients, based on molecular theory.

A theory of transport processes, concerned specifically with molten salts, has been recently proposed by Rice [5]. Rice considers an

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1. Collins & Raffael, J.Chem.Phys., 29, 699 (1958)
2. Green, in "Handbuch der Physik", editor Flugge, Vol.10, Springer-Verlag OHG, Berlin (1960)
3. Rice & Frisch, Ann.Rev.Phys.Chem., 11, 187 (1960)
4. Kirkwood, J.Chem.Phys., 14, 180 (1946)
5. Rice, Trans. Faraday Soc., 58, 499 (1962)

"ideal ionic melt" consisting of oppositely charged ions of equal size and identical properties (except for the sign of the charges), and thereby reduces the system to an equivalent one-component system. The assumption is made that hard-core encounters between like ions can be neglected, because configurations in which like ions of the same size closely approach one another have prohibitively high energy associated with them. The fundamental dynamic event is taken to be a hard-core collision of a pair of ions followed by quasi-Brownian motion under the influence of the fluctuating field due to the neighbouring ions. Utilising a series of plausible but not proven assumptions, it is considered that only short-range forces are important in transport processes. Thus, on the basis of the isoelectronic nature of argon, K^+ and Cl^- ions, Rice compares the viscosity, self-diffusion and thermal conductivity of molten KCl to that of liquid argon. Despite the very large difference in the temperatures at which the two liquids exist, moderately good agreement is found.

Other theoretical treatments of interest in this respect are those due to Kubo [1] and Bearman [2]. These treatments, and that of Rice, are mechanistic descriptions of transport processes at the molecular level.

A different approach to transport processes is the non-specific macroscopic description, which leads to the linear phenomenological equations of transport. The basis of this type of approach is the general

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1. Kubo, J.Phys.Soc. Japan, 12, 570, 1203 (1957)
2. Bearman, J.Physic.Chem., 65, 1961 (1961)

theory of irreversible (non-equilibrium) thermodynamics. There are three basic postulates [1] of the theory, and the validity of these postulates determines the applicability of the theory to specific fluid systems.

Postulate I. "For a system in which irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the non-equilibrium system are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities." It is not, as yet, possible to delimit the domain of validity of postulate I. In practice the consequences of this postulate agree with most experiments carried out in the laboratory, except for systems with large gradients of thermodynamic functions and for turbulent and shock-wave systems.

Postulate II. "The fluxes are linear, homogeneous functions of the forces."

Many experimental relationships describing transport processes, which have been developed over a long period, include postulate II implicitly, for example Ohm's Law of electric conduction.

Postulate II can be expressed in the form

$$J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta \qquad \ldots(8)$$

where J_α are the fluxes, and the phenomenological coefficients, $L_{\alpha\beta}$, are independent of the forces X_β. The coefficients $L_{\alpha\alpha}$ (i.e. $\alpha = \beta$) relate conjugated forces and fluxes. In self-diffusion, for instance, the

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1: Fitts, "Nonequilibrium Thermodynamics", McGraw-Hill, U.S.A. (1962)

conjugated force and flux are the chemical potential gradient and flow of matter, respectively. The coefficients $L_{\alpha\beta}$ $(\alpha \neq \beta)$, the "cross-coupling coefficients", are related with cross-phenomena, such as thermal diffusion. The domain of validity of postulate II may be established by working out its consequences and comparing the results with those obtained experimentally. As in the case of postulate I, postulate II is observed to be valid for systems close to equilibrium. For high temperature fluid systems, such as molten salts, the linear relationship between the fluxes and forces may not be valid; this question has not yet been examined in detail.

Postulate III. "If the fluxes and forces are linearly related, and if the phenomenological coefficients are well defined, then the matrix of the phenomenological coefficients is symmetrical".

Thus, $L_{\alpha\beta} = L_{\beta\alpha}$. This equality is known as the Onsager reciprocal relationship [1÷3]. In some circumstances the matrix is not symmetric. For example, when an external magnetic field acts on a system, the reciprocal relationship becomes $L_{\alpha\beta}(B) = L_{\beta\alpha}(-B)$, where B is the magnetic induction. The validity of the Onsager reciprocal relationship has been examined in detail by Miller [4], who has concluded that the available data support the view that this relationship correctly describes the observed situation, within the limits of experimental error, for a wide variety of

1. Onsager, Phys.Rev., 37, 405 (1931); 38, 2265 (1931)
2. Casimir, Rev.Mod.Phys., 17, 343 (1945)
3. Fitts, "Nonequilibrium Thermodynamics", McGraw-Hill, U.S.A. (1962)
4. Miller, Chem.Rev., 60, 15 (1960)

systems.

Within the postulates above, no deductions can be drawn, from experimentally determined transport coefficients, concerning either structure of molten salts or mechanism of transport, without the assumption of a model of the system under consideration.

The theory of nonequilibrium thermodynamics is the basis of several theories of transport in molten salt systems, for example, the theoretical treatments of Klemm [1] and Laity [2-5]. This method of approach and the various formalisms of transport which have been proposed, has been the subject of considerable discussion [6], and it is not by any means established that this approach to transport processes is particularly relevant to molten salt systems.

Some more or less speculative comparisons of diffusive and conductive mechanisms of transport phenomena have been given by Borucka et.al.[7], Djordjevic and Hills[8], Bockris et.al.[9], Dworkin et.al.[10] and Bockris and Hooper[6].

Many discussions of transport properties have been based on the contention that the activation energy for transport of ions involves two factors:

1. Klemm, Z.Naturforsch., 8a, 397 (1953); 15a, 174 (1960)
2. Laity, J.Physic.Chem., 63, 80 (1959)
3. Laity, J.Chem.Phys., 30, 682, (1959)
4. Laity, Ann.N.Y.Acad.Sci., 79, 997 (1960)
5. Laity, Disc.Faraday Soc., 32, 172 (1961)
6. Bockris & Hooper, Disc.Faraday Soc., 32, 218 (1961)
7. Borucka, Bockris & Kitchener, Proc.Roy.Soc. (London), A241, 554 (1957)
8. Djordjevic & Hills, Trans.Faraday Soc., 56, 269 (1960)
9. Bockris, Crook, Bloom & Richards, Proc.Roy.Soc. (London), A255, 558 (1960)
10. Dworkin, Escue & Van Artsdalen, J.Physic.Chem., 64, 872, (1960)

(i) the energy (E_J) required for an ion to cross a potential energy barrier in order to move into a hole and (ii) the energy (E_H) required for the formation of a hole.

Thus $$E = E_J + E_H \quad \ldots(9)$$

where E is the overall activation energy for transport. The relative contributions to the activation energy for diffusion (for example), made by these two factors, is a matter of some dispute. Glasstone, Laidler and Eyring[1], have interpreted the activation energy as a potential energy barrier between two equilibrium (minimum potential energy) positions of a particle. This implies that in order to diffuse by movement into a vacancy, the diffusing particle must acquire sufficient energy to cross the potential energy barrier. In other words the energy of activation is largely the work done in moving into an adjacent vacancy (i.e. $E_J \gg E_H$). A similar interpretation has been proposed by Swalin [2] in his treatment of self-diffusion in liquid metals.

Swalin deduces an expression for the diffusion coefficient in which no explicit activation energy term appears, yet a plot of log D against (1/T) (where D is the self-diffusion coefficient and T the temperature), is, in theory, linear over (a relatively small) range of temperature. Now, most self-diffusion data obey a relationship of the form (Arrhenius equation):

$$D = D_o \exp(E/RT) \quad \ldots(10)$$

where D_o is a temperature independent constant and E is the activation energy.

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1. Glasstone, Laidler & Eyring, "The Theory of Rate Processes", McGraw-Hill, U.S.A. (1941)
2. Swalin, Acta Met., 7, 736 (1959)

Thus a plot of log D against 1/T gives, in general, a straight line of slope E. The corresponding activation energy type terms in Swalin's treatment is denoted by Q and is given by:

$$Q = 2RT \qquad \ldots(11)$$

The activation energy as defined by this equation is a linear function of temperature whereas the observed activation energies for molten salts are largely independent of temperature over small temperature ranges.

A rather different approach is that of Bockris et.al. [1], who suggest that the work of making a hole is the principal part of the energy of activation and the work of moving into the hole is negligible (i.e. $E_H \gg E_J$).

It would appear that the measurement of self-diffusion coefficients under applied potential gradients should provide a fairly definite answer to this point of mechanism, although such experimental measurements would be extremely difficult to carry out with high precision. If the activation energy for diffusion is due largely to the work done in movement into a hole, then the activation energy should be a function of the potential gradient. If, however, the activation energy is due mainly to the energy of formation of holes then variation of potential gradient should have almost no effect on the activation energy. Another possible experimental test appears to be a comparison of investigations of diffusion (and other transport processes) under conditions of (i) constant volume and (ii) constant pressure.

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1. Bockris, Crook, Bloom & Richards, Proc.Roy.Soc.(London), A255, 558 (1960)

On the basis of the Swalin hypothesis, the energy of activation at constant volume will approach the energy of activation at constant pressure. However, according to the theory of Bockris, Crook, Bloom & Richards, the energy of activation at constant volume would be small compared to that at constant pressure.

(b) Experimental Methods

Experimental methods, involving transport processes in molten salts, which have been employed in the elucidation of molten salt constitution, include measurements of electric conductance, viscosity, transport number, diffusion and diffusion potential, and investigations of electrode processes.

(1) Electric Conductance

The rate of migration of an ion in a molten salt would, intuitively, be expected to be dependent on the radius of the ion concerned; as a first approximation, an inverse dependence would be predicted. This being the case, a larger ion would have lower mobility than a small ion, and thus the overall electric conductance of a molten salt should be closely related to the effective radii of the current-carrying species. Let us consider a hypothetical salt containing only simple ions. If, on the addition of a second salt, complex ions were formed, then a manifestation of the formation of complexes (of radii greater than the radii of the simple ions) should be a relative decrease in equivalent conductance of the salt mixture. This kind of reasoning has been used in discussion of the con-

ductance of mixtures of KCl and $CdCl_2$ [1]. For this system, the conductance is not a linear function of composition. The large negative deviations (i.e. from linearity) were interpreted as being due to the formation of large, covalently bound complex anions of low mobility; ions suggested were $CdCl_4^{2-}$ and $CdCl_6^{4-}$.

For some molten salt systems, the equivalent conductance is close to a linear function of mole fraction. This behaviour has been regarded as evidence for the non-existence of complex ions in the salt mixtures concerned.

The conductances of some systems (generally in which the cations differ considerably in size), do deviate markedly from ideality but the formation of complex ions has been presumed not to take place. For example, for the system LiCl - KCl Van Artsdalen and Yaffe [2] observed negative deviations from additivity and a minimum in the conductance, but it appears extremely unlikely that the formation of complex ions occurs.

Conductance studies [3-6] have demonstrated fairly conclusively that changes in constitution of mixtures of molten salts are reflected in the activation energy for conductance. If the sizes of the conducting species in the melt change or if the interionic forces change, then ionic migration is restricted and a maximum of activation energy is found, in the composition

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1. Bloom & Heymann, Proc.Roy.Soc.(London), A188, 392 (1947)
2. Van Artsdalen and Yaffe, J.Physic Chem., 59, 118 (1955)
3. Karpachev, Stromberg & Poltoratzkaya, J.Gen.Chem. (U.S.S.R.) 5, 793 (1935)
4. Bockris, Kitchener, Ignatowitz & Tomlinson, Trans.Faraday Soc., 48, 75 (1952)
5. Bockris, Kitchener & Davies, Trans.Faraday Soc., 48, 536 (1952)
6. Harrap & Heymann, Trans. Faraday Soc., 51, 259-268 (1955)

range in which the structural change takes place.

(2) Viscosity

From both experimental measurement and theoretical considerations, by Dunn [1], Andrade [2], Eyring [3], Ward [4] and Barrer [5] (particularly), it has been shown that the viscosity (η) of liquids, including molten salts, varies with temperature according to the equation:

$$\eta = A \exp (E_v/RT) \qquad \ldots(12)$$

A is a constant for a particular liquid and E_v is the energy of activation for viscous flow. Conductance of salts (of the uni-univalent type at least) is determined mainly by the smaller ion, because it will presumably have the higher mobility. The viscosity, however, is dependent upon the shearing forces between the larger ions and groups. For this reason, from the values of viscosities of molten salts and their mixtures, information relating to the nature of large anions, or complex ions, is obtainable. The formulation of a possible structure of molten salts should in principle be deducible from a correlation of activation energies for viscous flow and for conductance.

Values of the viscosities, alone, for molten salts or salt mixtures do not necessarily offer evidence for the existence of complex ions in the salts under consideration. For example, it was found by

1. Dunn, Trans.Faraday Soc., 22, 401 (1926)
2. Andrade, Phil.Mag., 17, 698 (1934)
3. Eyring, J.Chem.Phys., 4, 283 (1936)
4. Ward, Trans.Faraday Soc., 33, 88 (1937)
5. Barrer, Trans. Faraday Soc., 38, 322 (1942)

Harrap and Heymann [1] that for the systems $CdCl_2$ - KCl and $PbCl_2$ - KCl, neither the viscosity isotherms nor the isotherms of activation energy for viscous flow showed maxima, and hence from this work there was no evidence to suggest the presence of complex ions in the salts. This is in direct contrast to much of the experimental data for these two systems (e.g. conductance) which can be interpreted quite convincingly in terms of complex ion formation.

(3) Transport Number

Investigations of transport numbers of molten salts and their mixtures are discussed in Chapter 2 of this thesis.

(4) Diffusion

Angell and Bockris [2] have measured the diffusion coefficient of a cadmium radioisotope in molten mixtures of $CdCl_2$ and KCl. The interpretation of their results in the light of a number of structural models for the molten salt led to the conclusion that molten $CdCl_2$ contains associated entities which dissociate increasingly on addition of KCl. In respect of this work, it must be recognised that the measured diffusion data of Angell and Bockris were extremely inaccurate, and hence little weight can be attached to the interpretation which they proposed.

The usefulness of diffusion measurements in elucidation of the structure of molten salts is particularly important when diffusion data is considered in conjunction with other transport data. For instance, the

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1. Harrap & Heymann, Trans.Faraday Soc., 51, 259, 268 (1955)
2. Angell & Bockris, Electrochimica Acta, 1, 308 (1959)

comparison of diffusion and conductance data for pure NaCl led Borucka et.al.[1] to the conclusion that ionic migration in NaCl may take place by means of pairs of unlike ions moving, via "coupled vacancies", in the same direction. Such a mechanism of migration makes no contribution to the conductance of the salt, and thus these authors were able to offer a reasonable explanation for the apparent failure of the Nernst-Einstein equation, in molten salts.

(5) Diffusion Potential

The measurement, significance, etc. of diffusion potentials of molten salt systems are discussed at length in Chapter 3 of this thesis. It is noteworthy, that this property of molten salts has been scarcely investigated in the past, probably because theoretical understanding of diffusion potentials has been lacking to date.

(6) Electrode Processes

Electrode processes in molten salts have been investigated by a number of methods, including voltammetric (polarographic) and chronopotentiometric techniques, and the various pulse or transient methods.

In a circuit containing an electrode which is in contact with a molten salt electrolyte, the potential of the electrode depends upon the rate of diffusion of ions with which the electrode is in equilibrium, to the electrode-electrolyte interface. Thus, the variation with time of the electrode potential during a transient depends upon the variation in

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1. Borucka, Bockris & Kitchener, Proc.Roy.Soc. (London), A241, 554 (1957)

concentration of the species with which the electrode is in equilibrium. The concentration of these species can, therefore, in principle be determined. Such determinations allow distinction to be made between changes in concentration, of species in the bulk of a solution, due to all causes (indicated by direct measurement of thermodynamic activity perhaps), and changes in concentration due to complex ion formation. Analysis of the transients allows both the formula and concentration of each complex ion to be deduced.

By such methods, Inman and Bockris [1] were able to deduce values of the successive formation constants for complexes of Cd^{2+} with halide ions, in the $NaNO_3$ - KNO_3 eutectic solvent.

In conclusion, it has been stated [2] that the use of Raman spectral and electrochemical methods "...if carried out over a temperature range and combined with reversible E.M.F. studies .... would yield formula, concentration, dissociation constant, lifetime and heat or entropy of formation of the entities present (in molten salts)".

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1. Inman & Bockris, Trans.Faraday Soc., 57, 2308 (1963)
2. Bloom & Bockris, in "Fused Salts", editor Sundheim, Chapter 1, McGraw-Hill, U.S.A. (1964)

CHAPTER 2

THE MEASUREMENT AND SIGNIFICANCE OF TRANSPORT NUMBERS IN MOLTEN SALTS

A. Introduction

In the aqueous solution of an electrolyte, electric current is carried through the solution by the ions into which the electrolyte dissociates. That fraction of the total current which is carried by an ion, i, is the transport number (or transference number) of the ion i (denoted by t_i). The transport number is expressed in terms of the velocities of migration of the ions, the velocities of migration being defined with respect to a fixed frame of reference. For the infinitely dilute aqueous solution, the "stationary" solvent is a satisfactory frame of reference. In the case of a solid electrolyte, the solid lattice may be taken as an internal reference frame. Provided that such a frame of reference can be assigned, then there are no conceptual difficulties in the definition of the ionic transport numbers of the electrolyte.

It is not possible to assign an intrinsic frame of reference in the definition and measurement of ionic velocities (and hence transport numbers) in molten salt electrolytes. If the (internal) electrodes of the system, for example, are chosen as reference frame, then the cation and anion transport numbers of a molten salt are not meaningful, as

pointed out by Swarz [1]. For, if one Faraday of electricity passes, then one gram-equivalent of both cation and anion are discharged at the cathode and anode respectively, and either $t_+ = 1$ and $t_- = 0$, or else $t_+ = 0$ and $t_- = 1$, depending on which electrode is chosen as the reference electrode. Further, in a molten salt electrolyte there is neither a "stationary" solvent nor a solid lattice available as frame of reference.

For molten salt electrolytes therefore, an external reference frame must be chosen and the ionic velocities and transport numbers defined with respect to this reference frame.. Such a reference frame can be set up where the fused salt is contained in two compartments, separated by a diaphragm permeable to the ions of the electrolyte, but which does not allow free bulk flow of the electrolyte between the two compartments. In this case, the porous diaphragm may be assigned as external frame of reference. Other reference frames which have been used are the walls of a cell and asbestos paper, sintered glass, or alumina strips. The transport numbers defined and measured in this way (i.e. with respect to an external reference frame) have been called "Äussere Überführungszahlen" by Klemm [2], as distinct from "Innere Überführungszahlen" which are the transport numbers relative to a (hypothetical) internal frame of reference.

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1. Swarz, Z.Elektrochem., 45, 740 (1939)
2. Klemm, Z.Naturforsch., 15a, 173 (1960)

Review of Previous Work on Transport Numbers

Four types of methods have been used for the investigation of electromigration and measurement of transport numbers, in molten salts:

(i) Hittorf-type methods. In these experiments electrolysis is performed in a cell with a porous disc which separates anode and cathode compartments. During or after electrolysis, the anolyte and/or catholyte, are analysed in one or more of the following ways: by (a) volume change, (b) weight change, (c) concentration change of one component (in the case of mixtures of salts) and (d) by changes in activity of radioisotopes.

(ii) Moving-boundary methods. A boundary is formed between two different salts or salt mixtures (in contact in a vertical tube), an electrode being placed at each end of the molten salt column. The rate of movement of the boundary, during electrolysis, is measured.

(iii) Electrophoretic methods. A strip of asbestos paper, sintered glass, or alumina, is impregnated with the salt, each end of the strip being in contact with a reservoir of salt. The reservoirs act effectively as electrode compartments. During electrolysis, the velocities of the ions in the strip are measured by following the change in distribution of radioisotopes in the strip. The strip is in effect a very large porous disc.

(iv) Pressure - E.M.F. methods. A sudden pressure difference is established between the two compartments of a Hittorf-type cell, filled with the same salt mixture in both compartments, the change in stationary electric potential being measured. This change in potential is a function of the transport numbers.

Methods (i) and (ii) yield transport numbers directly, while (iii) and (iv) yield ionic mobilities.

Hittorf-type Experiments.

In these experiments it is essential to either eliminate or else take into consideration, bulk flow of electrolyte due to a hydrostatic head of salt. Various cells which have been used are illustrated schematically in Figure 2.

Methods which involve prevention of flow due to a hydrostatic head are :

(a) the moving-bubble technique (Figure 2B),

(b) the electrode displacement technique, necessarily using liquid electrodes, (Figure 2C),

(c) the measurement of volume change in horizontal capillaries (Figure 2D),

(d) the use of ultrafine porous discs, in order to minimise hydrostatic flow (Figure 2A).

Methods which have taken into account bulk flow of electrolyte under a hydrostatic head are:

(e) the weight versus time technique,

(f) the height versus time technique.

The moving-bubble technique (method (a)) was first used by Duke and Laity [1] to measure the transport numbers in pure fused lead chloride.

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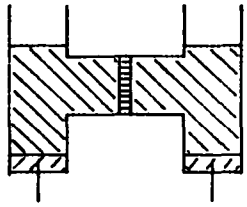
1. Duke and Laity, J.Amer.Chem.Soc., 76, 4046 (1954); J.Physic.Chem., 59, 549 (1955).

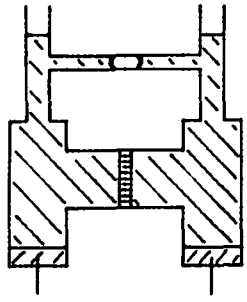
FIGURE 2

Schematic diagrams of cells used for Hittorf-type experiments based on volume changes.

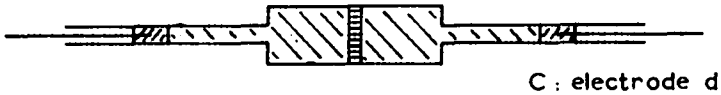
FIGURE 2



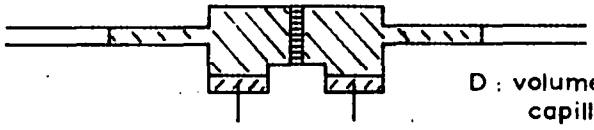
A : simple design.



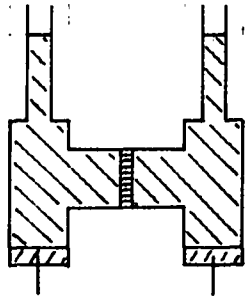
B : moving bubble.



C : electrode displacement.



D : volume change in horizontal capillaries.



E : volume change in vertical capillaries.

molten salt electrolyte.

electrode material, solid or fused.

porous disc.

The air bubble was trapped in the capillary when both parts of the cell were filled. During electrolysis the bubble moved slowly from the anode to the cathode compartment, and a weighed amount of lead chloride was added to the catholyte in order to make the bubble move in the reverse direction. The transport numbers were calculated from measurements of the time interval between the passings of the bubble along a vertical cross-hair on the capillary, before and after the $PbCl_2$ was added. These workers found that it was necessary to use ultrafine discs to obtain reproducible results. When medium or coarse porosity discs were used the bubble moved too slowly, indicating thereby one disadvantage of the method; evidently the bubble offered some resistance to motion. By using porous discs of different materials Duke and Laity showed that the transport numbers were independent of the material used. The same authors [1] measured the transport numbers in $PbBr_2$, TlCl and $AgNO_3$ by the same method, and Murgulescu and Marta[2] utilised this method to measure the transport numbers in $PbCl_2$.

Lorenz and Janz [3] studied the characteristics of gas bubbles in molten salts. They found that the force necessary to move a column of liquid along a glass capillary is considerable if the liquid does not wet glass (9.4 mm. for AgCl), whereas the force required is very small if the liquid

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1. Laity and Duke, J.Electrochem.Soc., 105 97 (1958)
2. Murgulescu and Marta, Acad.Rep.Pop.Rom.Stud. Cerc.Chem., 8, 375 (1960)
3. Lorenz and Janz, Jk Physic Chem., 61, 1683 (1957)

does not glass (0.9 mm. for $PbCl_2$). Thus a hydrostatic head may be present, for which a connection should be applied. Lorenz and Janz repeated Duke and Laity's experiments with an apparatus very similar to that used by Duke and Laity and found that with $PbCl_2$ almost all of the added salt transferred from catholyte to anolyte through the porous disc. If the disc was blocked off, and head of liquid built up until the bubble started to move, but once started, the hydrostatic pressure expelled the bubble completely from the tube. In addition, for small bubbles, Lorenz and Janz found a passage of electric current via the bubble. These findings indicate that the transport number data which have been obtained with the moving-bubble technique are quite inaccurate.

The electrode displacement technique (method (b)) was used by Bloom and Doull[1] to measure the transport numbers in $PbCl_2$ and $CdCl_2$. The movement of the boundary between (fused) lead metal and $PbCl_2$ was followed. There was no gravitational backflow, since no hydrostatic head was built up, the capillaries being perfectly horizontal. This work has been criticised by Lorenz and Janz[2]. The basis of their criticism appears to be: "In the electrode displacement technique as used by Bloom and Doull for molten $PbCl_2$, the displacement of the molten $PbCl_2$/ molten Pb interface was measured rather than displacement of the whole molten electrode. Molten Pb behaves similarly to molten AgCl, i.e., a relatively large pressure is

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1. Bloom and Doull, J.Physic.Chem., 60, 620 (1956)
2. Lorenz and Janz, J.Physic.Chem., 61, 1683 (1957)

required to initiate motion of a gas bubble. While the presence of the bubble is not obvious in the electrode displacement cell, a simple manoeuvre makes it apparent that a large bubble is present. If the two ends of the horizontal cell are imagined to be connected, the air space in the connecting arm may be visualised as one large bubble. The resistance to displacement of the lead electrodes would be relatively large in view of the similarity in behaviour to AgCl.... . ....the resistance to movement of the molten Pb in contact with the "large bubble" is as a whole greater than the resistance offered by the sintered diaphragm to the flow of molten salt as a liquid. Although the electrode displacement method appears to be sound in theory, the technique will lead to erroneous results unless the molten metal /gas interface is such that the molten metal shows no tendency toward "stickiness" in the transport cell." This criticism is entirely invalid, in the opinion of the present author. There is no bubble in the electrode displacement technique, in the same sense as there is a bubble in Duke and Laity's moving-bubble technique[1]. In the moving-bubble technique, a gas bubble is "constrained" between two horizontal columns of molten salt and therefore, to move the gas bubble it is necessary to displace both columns of liquid. In the electrode-displacement method, the system is open to the atmosphere, so that the electrode moves by displacement of air from the capillary, not against another column of melt, but against the (external)

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1. Duke and Laity, J.Amer.Chem.Soc., 76, 4046 (1954); J.Physic.Chem., 59, 549 (1955)

atmosphere. In principle, the atmosphere offers no resistance to such a displacement. To regard the electrode displacement cell used by Bloom and Doull [1] as being equivalent to one in which both ends of the cell are connected is, therefore, quite erroneous, because by connecting the two ends of the cell one applies constraints which are not present in practice. Hence the argument which is valid for a system with a "constrained" moving bubble does not apply to the open system used by Bloom and Doull.

Furthermore, since molten lead metal does not wet the material of the capillary (silica in this case), a thread of molten lead cannot offer any resistance to horizontal motion, just as a mercury thread in a horizontal glass capillary has zero resistance to motion (except where impurities are present either in the mercury or on the walls of the capillary). Thus the resistance to movement of the molten lead electrode would be extremely small, much smaller in fact, than the resistance offered by the sintered diaphragm to bulk flow of the molten salt as a liquid. A resistance to movement may appear in practice, due to impurities, (which wet the material of the capillary), in the lead; presumably resistance from this source would be very small as high purity lead was used in the experiments. Hence Bloom and Doull's measurements were valid not only in principle but also in practice.

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1. Bloom and Doull, J.Physic.Chem., 60, 620 (1956)

With a modification of Bloom and Doull's method, Bloom and James [1] dispensed with the moving electrodes by using electrodes which were fixed (solid silver, in measurements of the transport numbers of $AgNO_3$), and observing the movement of the air/salt interface in the capillary (method (c) above).

All methods discussed thus far were based on the measurement of a volume change, with a technique designed to eliminate flow under a hydrostatic head. Several experiments have been carried out [2-6] in which a simple cell, such as that shown in Figure A, with an ultra fine porosity disc, was used (method (d)). Duke and Cook [2] determined the tranpport number of silver in $AgNO_3$, with solid silver electrodes, and also the transport numbers in NaCl and KCl [3], using electrodes which were reversible to both anion and cation. Duke and Owens [4] measured volume changes in $LiNO_3$, $NaNO_3$ and KNO_3, by constructing cells of the type:

$$(+)\ Ag \mid AgNO_3 \mid MNO_3 \mid MNO_3 \mid AgNO_3 \mid Ag\ (-)$$

where M denotes an alkali metal, Duke, Laity and Owens [7, 8] made a complete analysis of transport numbers in a mixture of two fused salts. They measured volume changes, in vertical capillaries, in mixtures of

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1. Bloom and James, J.Physic.Chem., 63, 657 (1957)
2. Duke and Cook, Iowa State Coll. J. Sci., 32, 35 (1957)
3. Duke and Cook, ibid., 33, 81 (1958)
4. Duke and Owens, J.Electrochem.Soc., 105, 548 (1958)
5. Duke, Laity and Owens, ibid., 104, 299 (1957)
6. Duke and Owens, ibid., 105, 476 (1958)
7. Duke, Laity and Owens, J.Electrochem.Soc., 104, 299 (1957)
8. Duke and Owens, ibid., 105, 476 (1958)

$AgNO_3$ and $NaNO_3$ [1] and in mixtures of $AgNO_3$ and KNO_3 [2]. Their method had the disadvantage that an alternating current was superimposed on the direct (electrolysis) current, in order to prevent dendrite growth on the solid silver electrodes. The use of the alternating current gave rise to considerable heating and hence density changes. The method used by Duke and Victor [3], in their measurements of transport numbers in nitrate mixtures, was the determination of concentration changes in both compartments; each compartment contained a different salt, separated by an ultrafine porosity disc. The method is only useful, however, in those cases in which the cationic transport numbers of the two salts are equal or very nearly equal. If this condition is not fulfilled, a diffusion potential is established at the liquid junction between anolyte and catholyte, and cationic transport in one salt is either enhanced or retarded, depending on the relative magnitudes of the cationic transport number in the two salts.

Several experiments have been based on the measurement of changes in radiotracer concentration. Basically the cells used in all such methods have been of the type shown in Figure 2A. This type of technique has been used by Duke and co-workers [4-7] and Wolf [8] on the

1. Duke, Laity and Owens, J.Electro.Chem.Soc., 104, 299 (1957)
2. Duke and Owens, ibid., 105, 476 (1958)
3. Duke and Victor, J.Amer.Chem.Soc., 83, 3337 (1961)
4. Duke and Fleming, J.Electrochem. Soc., 106, 130 (1959)
5. Duke and Bowman, ibid., 106, 626 (1959)
6. Duke, Bowman, Wolf and Garfinkel, Ann.N.Y.Acad.Sci., 79, 1023 (1960)
7. Wolf and Duke, J.Electrochem.Soc., 110, 311 (1963)
8. Wolf, ibid., 108, 811 (1961)

salt systems $PbCl_2$ / KCl, alkali chlorides, AgCl and alkaline-earth chlorides. Murgulescu and Tapor have investigated $TlNO_3$ [1] and $CsNO_3$ [2], and Lunden [3] has measured transport numbers in $ZnCl_2$ by the radiotracer method.

Since the present work was carried out, methods of measurement of transport numbers have been devised, in which no attempt is made to eliminate bulk flow due to a hydrostatic head. Fundamentally, the methods involve the determination of weight or volume changes in the electrode compartments as a function of time, during electrolysis. At the same time bulk flow of the electrolyte resulting from a hydrostatic head, is taken explicitly into consideration. This type of method has the great advantage that it eliminates experimental difficulties and uncertainties associated with the complete elimination of "hydrostatic flow". By measuring changes in weight as a function of time, Kellogg and Duby [4,5] determined the transport numbers in $AgNO_3$, while Fischer and Klemm [6] investigated TlCl and $ZnCl_2$ by measuring volume changes as a function of time. A very similar method was employed by Labrie and Lamb [7] in their study of $NaNO_3$.

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1. Murgulescu and Tapor, Z.Phys.Chem.(Leipzig), 219, 134 (1962)
2. Murgulescu and Tapor, ibid., 221, 39 (1962)
3. Lunden, J.Electrochem.Soc., 109, 260 (1962)
4. Kellogg and Duby, J.Phys.Chem., 66, 191 (1962)
5. Duby, Diss.Abs., 23, 2711 (1963)
6. Fischer and Klemm, Z.Naturforsch., 16a, 563 (1961)
7. Labrie and Lamb, J.Electrochem.Soc., 110, 810 (1963)

Moving Boundary Experiments

Moving-boundary experiments have been performed by Klemm and Mense [1] on $PbCl_2$ / KCl mixtures, by Monse [2] on the $AgNO_3$/AgCl system and by Duke and Cook [3] on $PbCl_2$. The method has limited application, because there must be no concentration changes on either side of the boundary and the colours or refractive indices of the two salts or salt mixtures must be sufficiently different for the boundary between the two liquids to be observed. Furthermore, the two salts or salt mixtures must have very different densities, in order to form a boundary which is as close as possible to a mathematically sharp boundary.

Electrophoresis Experiments

The recent "paper" electrophoresis technique has been employed by Arnikar [4,5] to measure mobilities of alkali metal ions and halide ions in fused $NaNO_3$, and by Alberti, Grassini and Trucco [6]. The method has been used most recently by Forscheri and Monfini [7] and by Honig [8].

This appears to be an excellent method of measurement of transport numbers in molten salts, because measurements of high precision are possible and also because it is possible to determine ionic mobilities of species which are present in very low concentrations.

1, Klemm and Mense, Z.Naturforsch., 12a, 319 (1957)
2. Monse, ibid., 12a, 526 (1957)
3. Duke and Cook, J.Physic.Chemk, 62, 1593 (1958)
4. Arnikar, Thesis, Masson et Cie., Paris (1959)
5. Arniker, Compt.Rend. (Paris), 244, 2241 (1957)
6. Alberti, Grassini and Trucco, J.Electroanal.Chem., 3, 283 (1962)
7. Forscheri and Monfini, J.Physic.Chem., 67, 1566 (1963)
8. Honig, Thesis, Amsterdam (1964)

Pressure - E.M.F. Experiments

This recent technique has been used by Duby and Kellogg [1] on AgCl and $PbBr_2$. It appears to be a promising and reliable technique although it has not yet been extensively tested.

1. Duby and Kellogg, J.Electrochem.Soc., 110, 349 (1963)

Summary of Experimental Data on Pure Fused Lead Chloride

Type of Cell	Method of Measurement	Temperature	t-	Reference
1, asbestos disc	Analysis of the two compartments.	520-680	0.78±0.03	(2)
2. corundum dust diaphragm	Same as 1.	550-580	0.83	(3)
3. bubble cell	volume change, bubble displacement	565	0.758±0.014	(4)
4. bubble cell	Same as 3	635	0.757±0.008	(5)
5. horizontal cell	displacement of electrode / electrolyte interface	527-529	0.39± 0.01	(6)
6. same as 5	same as 5	602-608	0.38± 0.01	(6)
7. moving boundary cell, U-tube with fritted disc and capillary	displacement of electrolyte / electrolyte interface	550	0.76± 0.04	(7)
8. fritted disc and capillary	volume change, bubble displacement	not given	0.73± 0.03	(8)
9. horizontal cell, fixed electrodes	displacement of electrolyte / air interface	550 + 3 −	0.37± 0.01	this work

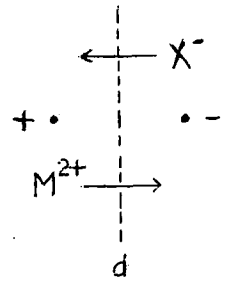
1. Duby and Kellogg, J.Electrochem.Soc., 110, 349 (1963)
2. Karpacher and Pal'guev, Zh.Fiz.Khim., 23, 942 (1949)
3. Delimarskii, Turov and Gitman, Ukrain.Khim.Zh., 21, 314 (1955)
4. Duke and Laity, J.Amer.Chem.Soc., 76, 4046 (1954)
5. Duke and Laity, J.Physic.Chem., 59, 549 (1955)
6. Bloom and Doull, J.Physic.Chem., 60, 620 (1956)
7. Duke and Cook, J.Physic.Chem., 62, 1593 (1958)
8. Murgulescu and Marta, Acad.Rep.Pop.Rom.Studii Cere.Chim., 8, 375 (1960)

Present Investigation

In the present work a technique based on those of Bloom and Doull[1] and Bloom and James[2] has been employed to measure the transport numbers in pure fused lead chloride. The electrodes were fixed, as in the method of Bloom and James, in order to preclude errors arising from possible resistance to motion of the lead electrodes in the glass capillaries. The volume changes in anolyte and catholyte were determined by measuring the displacement of the air / electrolyte interfaces in the horizontal capillaries.

Calculation of Transport Number from Volume Change

The experimental cell can be represented symbolically as:



d represents the porous disc

. represents the lead metal electrodes

($M^{2+} = Pb^{2+}$, $X = Cl^{-}$, in this particular case)

Assume that the salt MX_2 is ionised into M^{2+} and X^- ions only. Let j Faradays of electricity be passed through the electrolyte. In the anode compartment j equivalents of X^- ions deposit at the anode, discharge and liberate j equivalents of X^- ions and j equivalents of M^{2+} (by dissociation of the j equivalents of MX_2 formed). Further, if t_- and t_+ are the transport numbers of anion and cation, then jt_- equivalents of X^- ions diffuse from catholyte to

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1. Bloom and Doull, J.Physic Chem., 60, 620 (1956)
2. Bloom and James, J.Physic Chem., 63, 757 (1959)

anolyte and $j.t_+$ equivalents of M^{2+} ions diffuse from anolyte to catholyte.

If V_{X^-} is the volume of one equivalent of X^- ions in liquid MX_2, V_M the volume of one equivalent of M in the anode metal, and $V_M{}^{2+}$ the volume of one equivalent of M^{2+} ions in liquid MX_2, then the change in volume of the anode compartment, ΔVa, is given by :

$$\Delta Va = (j.t_- V_{X^-}) - (jt_+ V_M{}^{2+}) + (j.V_M{}^{2+}) - (j.V_M) \quad \ldots(1)$$

In the cathode compartment, j equivalents of M^{2+} ions are deposited on the cathode, $j.t_-$ equivalents of X^- ions diffuse from catholyte to anolyte and $j.t_+$ equivalents of M^{2+} ions diffuse from anolyte to catholyte. Hence, the change in volume, ΔV_C, of the catholyte is given by :

$$\Delta V_C = -(j.V_M{}^{2+}) + (j.V_M) - (j.t_-.V_{X^-}) + (j.t_+.V_M{}^{2+}) \quad \ldots(2)$$

From equation (1)

$$t_- = \frac{j.V_M + \Delta V_a}{j\,(V_M{}^{2+} + V_{X^-})} = \frac{j.V_M + \Delta V_a}{j.V_{MX_2}} \quad \ldots(3)$$

Where V_{MX_2} is the volume of one equivalent of liquid MX_2.

From equation (2)

$$t_- = \frac{j.V_M - \Delta V_C}{j.V_{MX_2}} \quad \ldots(4)$$

Both equations (3) and (4) can be used to deduce the anion transport number from the experimentally measured quantities ΔV_a and ΔV_C. The cation transport number t_+ follows from the relation

$$t_+ + t_- = 1 \quad \ldots(5)$$

The total volume change in the cell,

ΔV_T, is given from (3) and (4) by

$$\Delta V_T = \Delta V_a + \Delta V_c = 0 \quad \ldots(6)$$

Thus it is not possible to determine transport numbers by using a cell in which bulk flow of the salt, between anolyte and catholyte, is not inhibited (by a porous membrane, for example), because in such a case the total volume change ΔV_T is, in principle, the only measurable volume change, and by equation (6) ΔV_T is zero.

Objects of the Present Work

The aims of this work were two-fold: (a) to resolve the uncertainty in previously measured transport numbers in pure $PbCl_2$ and (b) to elucidate, if possible, the mechanism of ionic transport and the nature of the species involved in the transport processes.

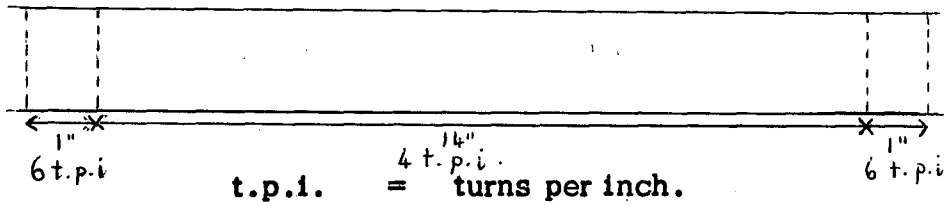
A theoretical treatment of transport numbers in molten salts has been devised also, which allows calculation of these quantities on the basis of various structural models and mechanisms of ionic transport.

B. Experimental

1. Apparatus

(a) Furnace

A schematic diagram of the furnace is shown in Figure 3. The block of the electric resistance furnace was a transparent silica tube, F, 16 ½" long, 1" inside diameter and 1¼" outside diameter. The tube was wound with Kanthal A, B and S 25 gauge, resistance wire, in the manner shown below:



t.p.i. = turns per inch.

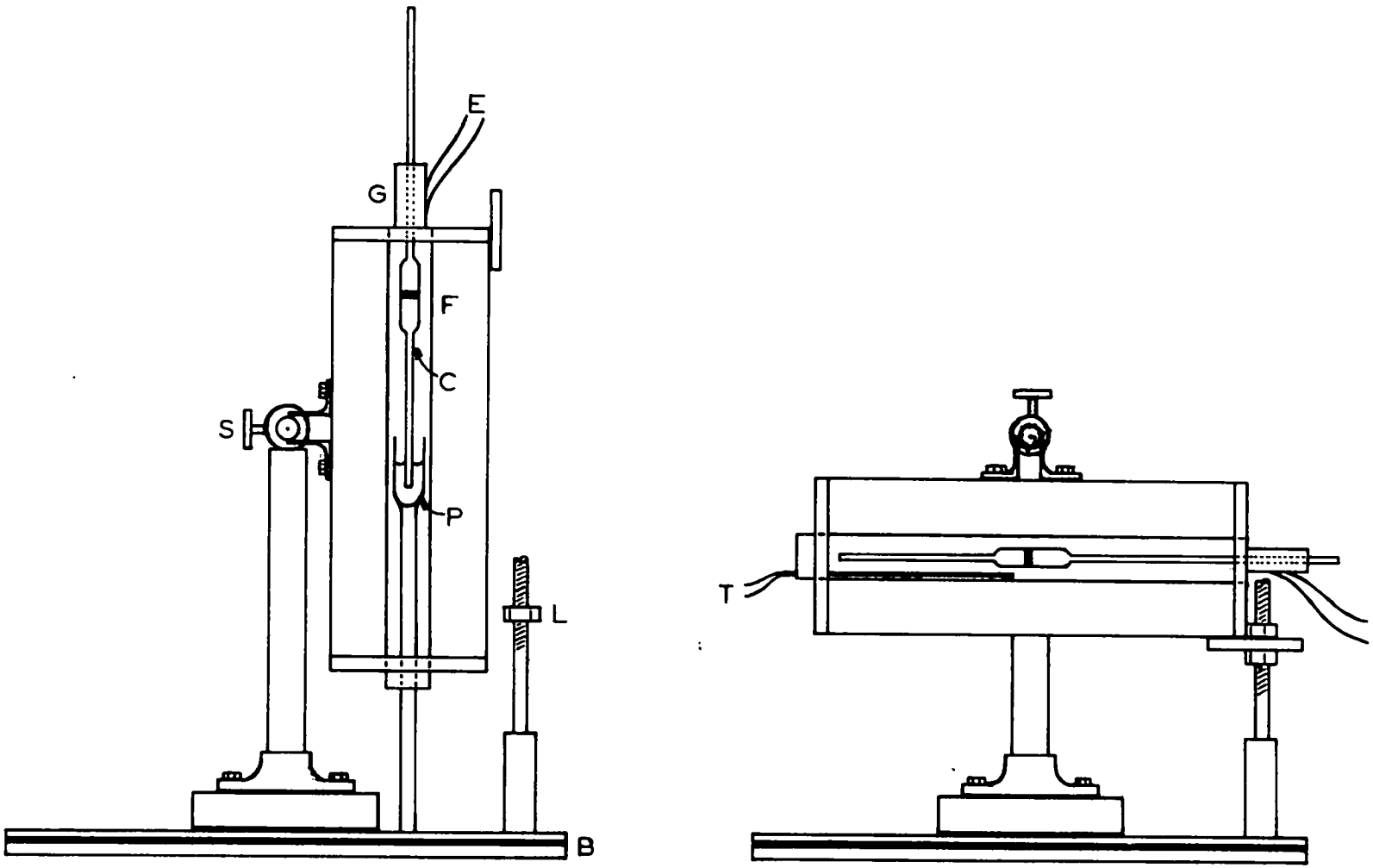
It was found that such a winding scheme gave a uniform temperature, to within 1 - 2° C, over the central 10" (approximately) of the furnace tube. The windings were held in place by two ½" wide strips of high alumina content refractory cement. A coil of 45 s.w.g platinum wire was wound between the coils of the heating element and functioned as a temperature sensing element (see Temperature Control).

The furnace case consisted of a frame of ¾" x ¾" x ⅛" angle iron of dimensions 6" x 6" x 16", and sides of ¼" thick "Sindanyo" asbestos sheet. A 3/16" wide slot formed by two "Sindanyo" sheets allowed viewing of the centre of the furnace tube. The slot was illuminated from one side of the furnace by a 125 watt tubular incandescent lamp, and was

FIGURE 3.

Furnace used in transport number measurements.

FIGURE 3



a

b

covered at each end by a thin sheet of ruby mica, to reduce heat losses from the furnace tube via the slot. The furnace case was packed with asbestos "wool" lagging.

The furnace was supported at a point mid-way along one side by a $\frac{3}{4}$" diameter silver steel rod, so that it could be held in either a horizontal or a vertical position. Figure 3 shows the cell in (b) the horizontal and (a) the vertical position. It was locked in position, whenever necessary, by a screw, S. The steel supporting rod was carried by two brass bushes, each of which was welded to a tubular steel column. The columns were bolted to a heavy wooden base B, which was covered with a sheet of $\frac{1}{4}$" thick "Sindanyo" sheet. In the horizontal position, the level of the furnace was adjusted by means of a fine-threaded levelling screw, L.

A brass block, G, attached to the upper end of the furnace case, allowed the cell (c) to be held in any required position in the furnace (see description of Cell).

A thermocouple, T, was inserted and held in the lower end of the furnace, for the measurement of temperature while experiments were in progress.

A silica pot, P, contained the molten salt for filling of the cell (see Experimental Procedure)

The power supply to the furnace was stabilised by a 1 K.V.A. voltage stabiliser and controlled by a "Variac" variable transformer.

(b) Cell

A schematic representation of the (Hittorf - type)

transport cell is shown in Fig. 4. The cell (c) was constructed from Pyrex glass, the porous discs, D, being cut from discs of sintered Pyrex of nominal porosities 2, 3 and 4 ("medium", "fine" and "very fine"). The bulb of the cell was 2" long and 1/2" in diameter. The lengths of the upper and lower capillaries (I) were 9" and 7" respectively. The capillaries were both 3/16" in diameter and their bores varied from cell to cell, between o.o3913 cm. and 0.05126 cm.

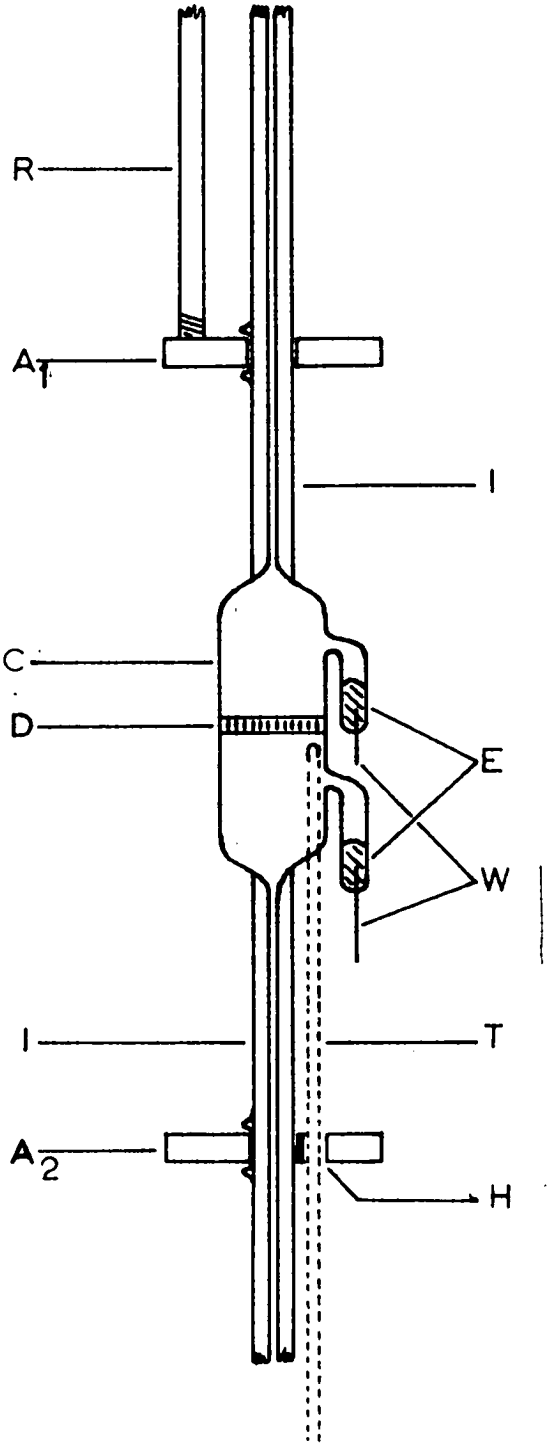
The lead metal electrodes, E, were contained in small side-tubes as shown. Contact with the electrodes E was established by two 0.016" diameter wires, of composition 50% tungsten / 50% molybdenum, sealed into the side-tubes. Each of these wires was welded to a 24 s.w.g. "A" nickel lead (E, in Figure 4). The nickel leads passed out of the furnace via its upper end and were connected to the current supply / measurement circuit.

The cell was supported in the furnace by a simple device which consisted of a 3/16" diameter stainless steel rod, R, screwed into a Sindanyo disc, A_1. The cell was held in the disc A_1 by two small protuberances on the upper capillary of the cell (Figure 4.) Rod R passed through a hole in the brass block (G , Figure 3) attached to the upper end of the furnace case. When necessary the cell was held in position by clamping rod R, with a small screw, in the brass block. The lower end of the cell was supported by a second "Sindanyo" disc, A_2, which was held,

FIGURE 4.

Transport number cell used in present work.

FIGURE 4



as before, between two small protuberances on the capillary. This disc had a hole H, drilled through it, which allowed the thermocouple (T) to be placed in position with its hot junction in the vicinity of the porous disc.

The diameters of the discs A_1 and A_2 were $\frac{7}{8}$", i.e. $\frac{1}{8}$" less than the inside diameter of the furnace tube. Thus, when in position in the furnace, practically no lateral movement of the cell was possible. Furthermore, the discs acted as effective radiation baffles, thereby reducing heat losses via the ends of the furnace tube.

All cells were so constructed that the two capillaries were accurately linear.

(c) Temperature Measurement

The temperature was measured with a Platinum - Platinum / 13% Rhodium thermocouple, in conjunction with a Leeds and Northrup 8686 Millivolt Potentiometer. The hot junction of the thermocouple was located at a point approximately $\frac{1}{16}$" from the outside of the cell, in the vicinity of the porous disc.

The 26 s.w.g. thermocouple wires were contained in a $12\frac{1}{2}$" x $\frac{1}{8}$" x $\frac{3}{32}$" double-bore alumina insulator. The cold junction was constructed by soldering two copper leads to the thermocouple wires, these junctions being maintained at 0° C. The thermocouple was calibrated at the following thermometric fixed points:

Freezing point of (A.R.) cadmium	320.9° C
Freezing point of (A.R.) zinc	419.45°C
Freezing point of (electrolytically pure) silver	960.5°C
Freezing point of (A.R.) sodium chloride	800.1°C

(d) Temperature Control

The temperature of the furnace was controlled in two ways. First, with a temperature control unit consisting basically of an AC bridge, one arm of which was the coil of very fine (45 S.W.G.) platinum wire (of resistance approximately 45 ohms at room temperature). The coil of platinum wire was wound on the furnace tube in close proximity to the heating elements. The circuit diagrams for the unit are reproduced in Figures 5 (a) and (b) [1]. By employing this device it was possible to keep the furnace temperature constant to within ± 0.02°C (at 550° C) for as long as required. In all but three experiments the temperature was controlled in this way.

The second method of temperature control used was as follows: The power supply to the furnace was adjusted (by means of the "Variac") to give the desired furnace temperature. After a few hours, thermal equilibrium between the furnace and its surroundings was established, and thereafter there was no measurable variation in furnace temperature.

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1. The temperature control unit was designed and built by Mr.D.E.Millwood (University of Tasmania)

FIGURES 5 (a) and (b).

Circuit diagrams for temperature control unit. The units of capacitance are microfarads unless otherwise stated. The units of resistance are ohms, except that K denotes ohms x 10^3 and M denotes ohms x 10^6 .

FIGURE 5(a)

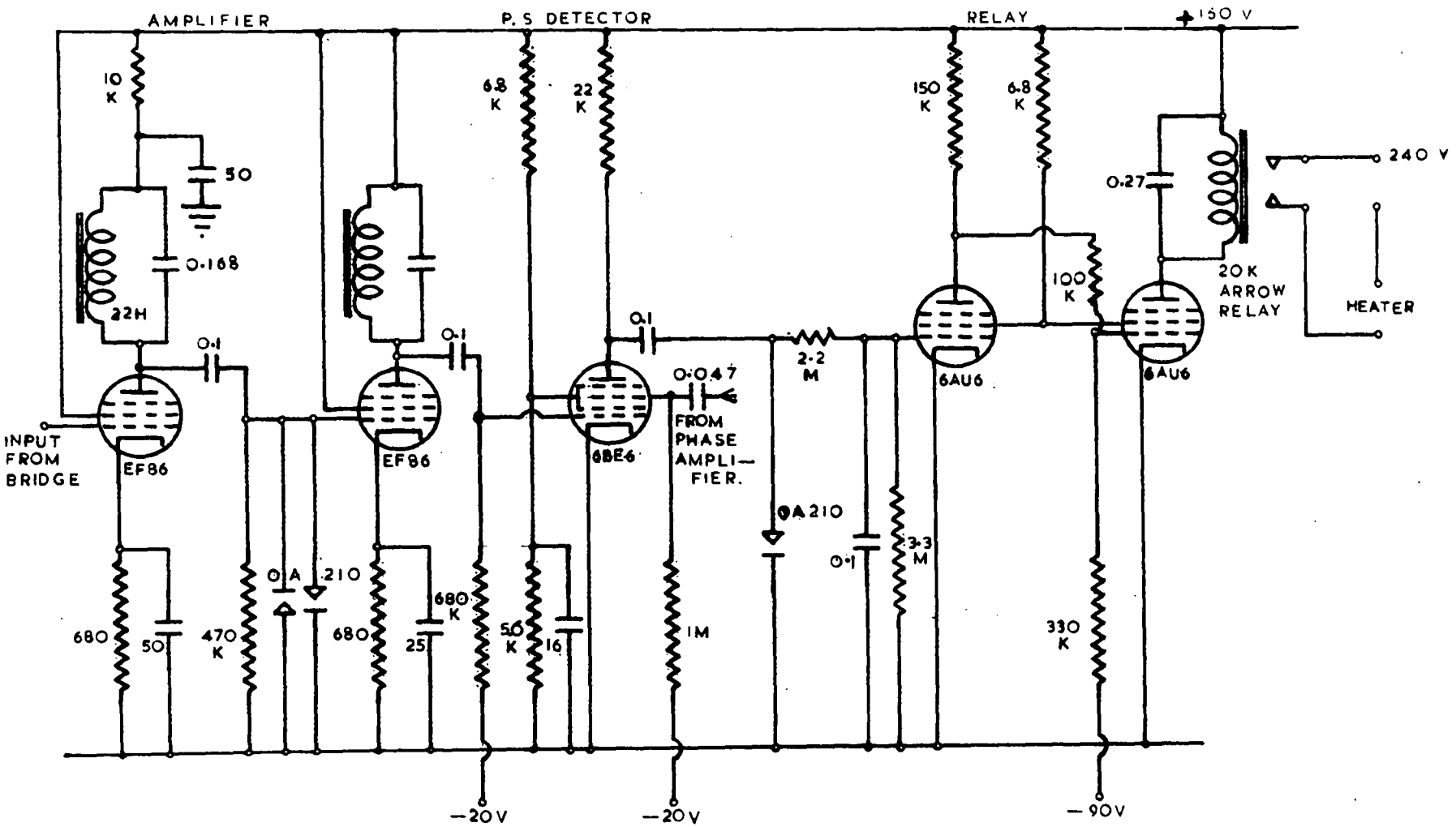
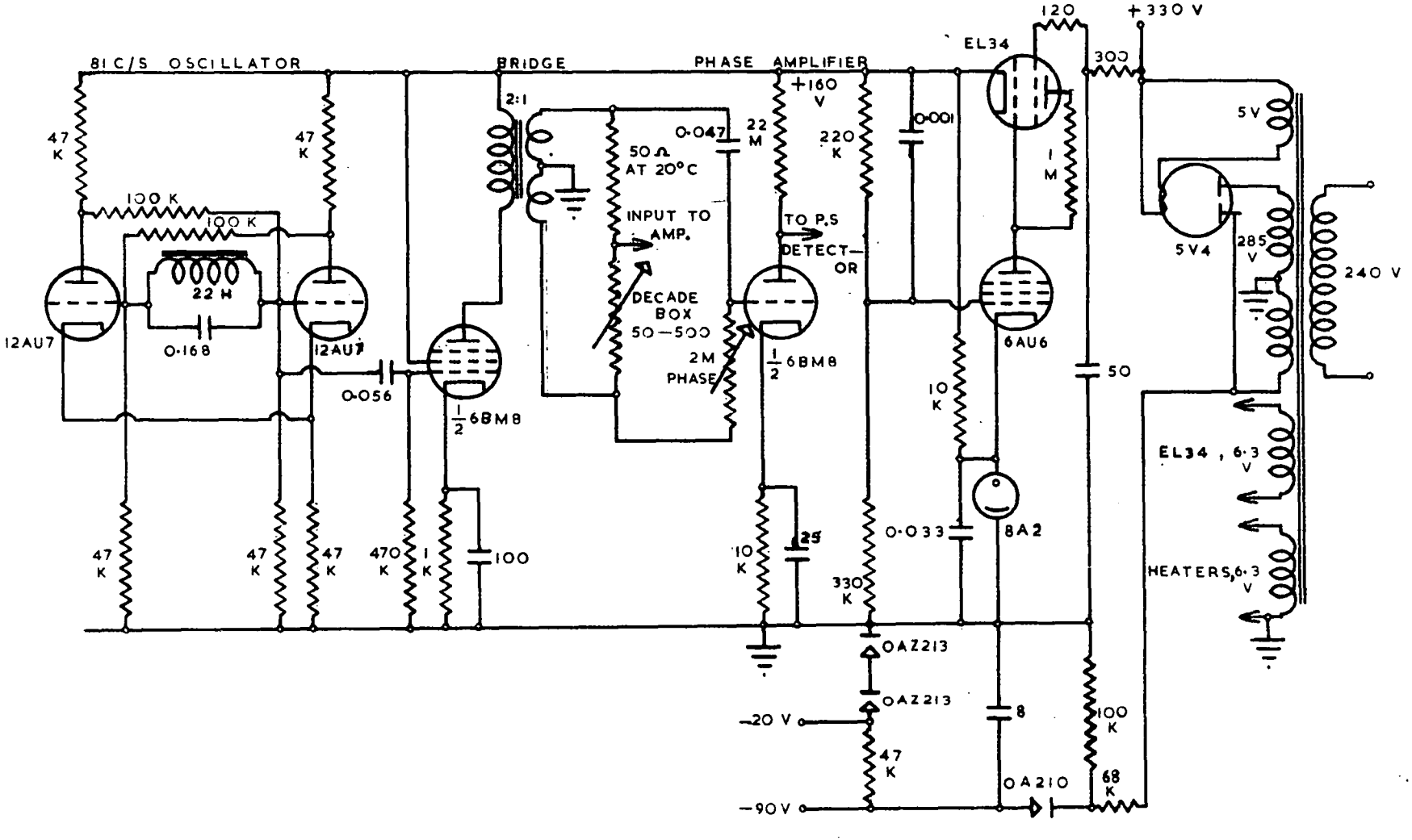

AMPLIFIER
P.S DETECTOR
RELAY
+150 V
10 K
50
0·168
22H
0·1
EF86
INPUT FROM BRIDGE
680
50
470 K
0·1
0·1
EF86
680
680 K
25
50 K
16
0·1
6BE6
0·047
FROM PHASE AMPLI— FIER.
1M
6·8 K
22 K
2·2 M
OA210
0·1
3·3 M
150 K
6·8 K
6AU6
100 K
330 K
0·27
20K ARROW RELAY
6AU6
240 V
HEATER
−20V
−20V
−90V

FIGURE 5(b)


81 C/S OSCILLATOR
BRIDGE
PHASE AMPLIFIER
EL34
+330 V
120
300
47 K
47 K
100 K
100 K
22 H
0·168
12AU7
12AU7
0·056
2:1
50 Ω AT 20°C
0·047
22 M
INPUT TO AMP.
DECADE BOX 50—500
2M PHASE
+160 V
220 K
TO P.S
DETECT—OR
0·001
1 M
5V
5V4
285 V
240 V
6AU6
10 K
50
8A2
0·033
330 K
EL34 , 6·3 V
HEATERS, 6·3 V
1/2 6BM8
1/2 6BM8
47 K
47 K
47 K
470 K
1 K
100
10 K
25
OAZ213
OAZ213
-20 V
47 K
-90 V
8
100 K
OA210
68 K

It was essential to control the furnace temperature very closely, because the air-salt interface displacements measured during electrolysis were very small (0.0050cm. - 0.1300cm.) and small fluctuations in furnace temperature (of the order ± 1 - 2°C, for example) would have caused volume changes of a similar magnitude.

(e) Current Measurement

The electrolysis current was determined by measuring the voltage drop across a known resistance, with a Cambridge Vernier Potentiometer. A calibrated Pye Decade Resistance Box, of specified accuracy ± 0.02% was used as the known resistance. In general, the magnitude of the resistance was 10 ohms, so that the voltage drop across it was of the order 100 millivolts.

The time for which the current was passed through the cell was measured with a laboratory stop-clock.

(f) Current Source

It was necessary for the electrolysis current to be constant within very close limits, because the amount of electricity passed during electrolysis was calculated on the assumption that the current flowing was constant during the measured length of time. An alternative procedure could have been used, for example measurement of the amount of electricity with a coulometer, but the procedure used was simpler to carry out in practice and was not subject to appreciable error.

A circuit diagram of the current source

is reproduced in Figure 6.[1] The output could be varied between 0 and 20 milliamps. The high stability of the instrument is illustrated by the fact that the variation in current for a change of 20 volts in input voltage (230 v. mains) was no more than 5 parts in 10^4. Since the input was stabilised by a voltage stabiliser, the variation in practice was less than 1 part in 10^4. The output variation for loads between 0 and 1000 ohms was not greater than 1 part in 10^4, so that the electrolysis current was constant to within 0,02%

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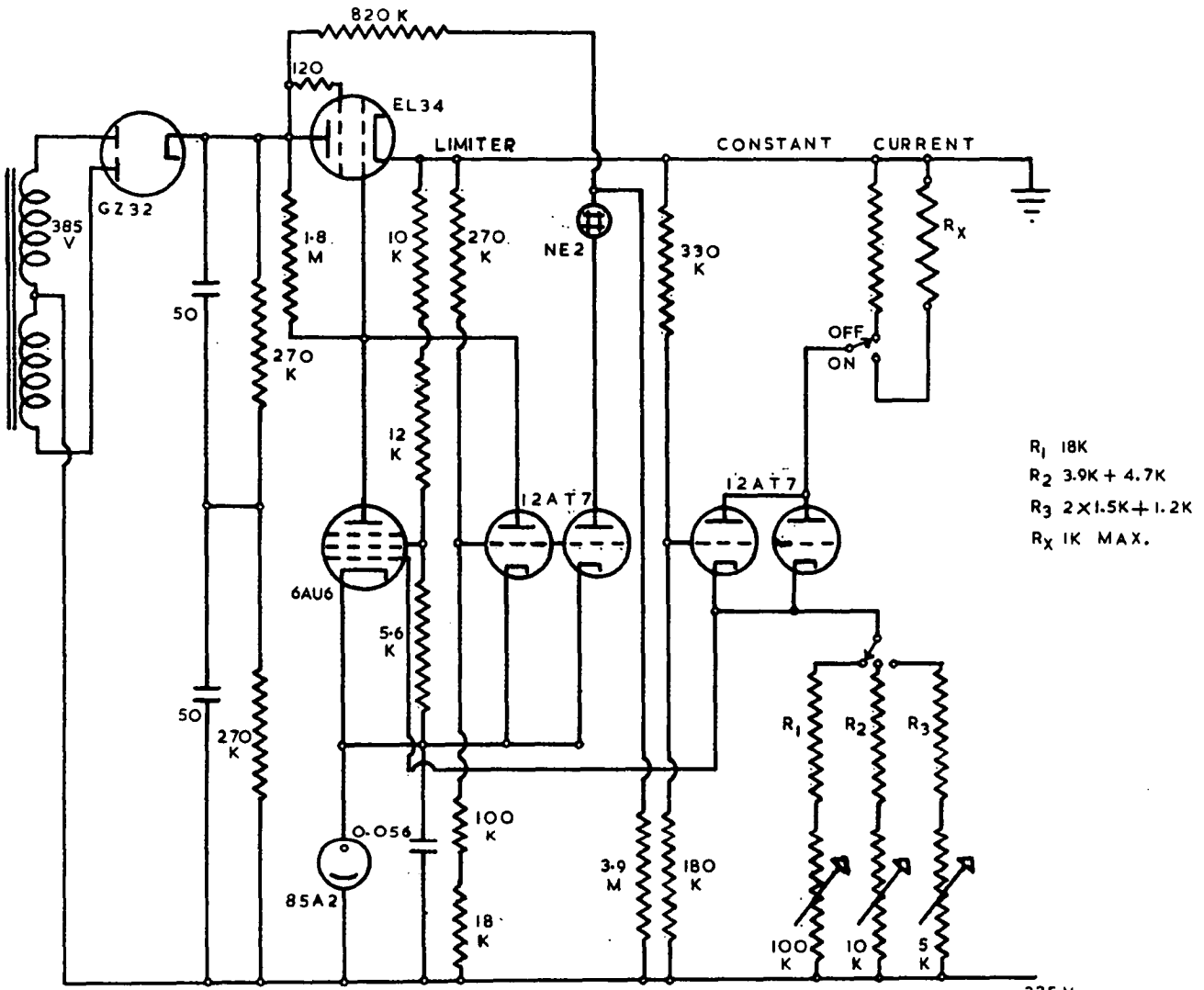
1. The current source was designed and built by Mr.D.E.Millwood (University of Tasmania)

FIGURE 6.

Circuit diagram for current supply unit. The units of capacitance are microfarads unless otherwise stated. The units of resistance are ohms, except that K denotes ohms x 10^3 and M denotes ohms x 10^6.

FIGURE 6


820 K
120
EL34
LIMITER
CONSTANT
CURRENT
385 V
GZ32
1·8 M
10 K
270 K
NE2
330 K
R_X
OFF
ON
50
270 K
12 K
12AT7
12AT7
6AU6
5·6 K
50
270 K
R_1
R_2
R_3
0·056
100 K
3·9 M
180 K
85A2
18 K
100 K
10 K
5 K
−235 V
R_1 18K
R_2 3.9K + 4.7K
R_3 2×1.5K + 1.2K
R_X 1K MAX.

2. Materials Used in the Experiments

The lead chloride used in the experiments was made by the method of Bloom and Heymann [1], from $Pb(NO_3)_2$ (May and Baker Ltd. "Analar" grade) and hydrochloric acid (Ajax Chemical Pty. Ltd. "Analar" grade). The $PbCl_2$ was kept in an oven at 120° C when not in use.

The lead metal used was May and Baker Ltd. "Analar" grade lead foil. This material was found to possess generally a surface film of oxide and was therefore purified before use, by shaking the fused metal in an atmosphere of hydrogen, to reduce the oxides to lead.

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1. Bloom and Heymann, Proc. Roy.Soc. (London), A188, 392 (1947)

3. Experimental Procedure

In the construction of the cells, an open side-arm was attached to the bulb of each cell (on one side of the porous diaphragm). Through this side-arm small pieces of purified lead were dropped into a side-tube (see Figure 4), and the side-arm was then drawn off at the surface of the cell. The cell was subsequently evacuated and the lead melted. While the lead was molten, the vacuum was suddenly released and the molten lead thereby forced into intimate contact with the electrode wire.

To fill the cell with molten lead chloride, it was clamped in the (vertical) furnace which was maintained at a constant temperature (550°C) The lower end of the cell dipped into a silica pot (P in Figure 3) containing molten lead chloride. To admit salt into the cell, the upper end of the cell was connected to a vacuum pump and molten salt drawn into the cell, until the salt solidified in the upper capillary, only a small portion of which was in the hot zone of the furnace. The salt container was then removed from the furnace, the vacuum released and the furnace rotated to the horizontal position. The cell was moved into the centre (uniform temperature portion) of the furnace and again clamped in position. After the salt (which had solidifed in the capillary) melted the level of the furnace was adjusted with the levelling screw until the cell was approximately horizontal. While the system was attaining thermal equilibrium the thermocouple was placed in position and lead deposited

by electrolysis, on the electrode devoid of lead. It was found that during this period any small air bubbles in the cell were completely absorbed by the melt. When the temperature (indicated by the thermocouple) became invariant, the cell was exactly levelled with the levelling screw. Levelling was accomplished as nearly as possible, by sighting the centre of each capillary with a travelling microscope (which was itself mounted on a precisely horizontal base.) The cell was presumed to be exactly horizontal when no movement of one salt / air interface could be detected, with the travelling microscope, over a period of at least two hours.

Currents of from 4.5 to 15 milliamps (approximately) were passed, for periods of up to $2\frac{1}{2}$ hours, during which time the displacement of one or both menisci was measured with the microscope. The direction of current flow was then reversed and the measurements repeated. This procedure was carried out for as long as possible, the time available for observation being limited by the tendency for the capillaries to sag appreciably after long periods in the furnace (not less than 10 - 12 hours, at 550°C).

At the conclusion of each experiment, the cell was removed from the furnace and allowed to cool to room temperature. Each cell was used for only one experiment.

The radii of the capillaries were measured before an experiment by weighing a thread of purified mercury, whose lengths in the

capillaries had been measured with the microscope. From the known density of mercury at the corresponding room temperature, the capillary radii were calculated.

Measurements of transport number were carried out in cells whose discs varied in porosity from 2("coarse") to 4 ("very fine"), in order to establish whether the values obtained were dependent on disc porosity. For a similar reason both the electrolysis current and time of electrolysis were varied, in order to gauge the influence (if any) of these factors on the measured transport numbers. The currents used were always small (not greater than 15 milliamps) in order to avoid Joulean heating of the porous disc.

C. Results

The anion transport number in pure fused lead chloride, at 550± 3 °C, was calculated from the equations:

$$t_- = \frac{j\,V_M + \Delta V_a}{j\,V_{MX_2}}$$

$$t_- = \frac{j\,V_M - \Delta V_c}{j\,V_{MX_2}}$$

Where the symbols have the same significance as before (page 55).

The values used for V_{MX_2} and V_M were derived as follows:

V_{MX_2} is equal to (0.5 x molar volume of $PbCl_2$). The molar volume at the appropriate temperature was calculated from the accurate density measurements of Boardman et. al., [1] and V_M was computed similarly, from the values for the density of lead metal, determined recently by Kirshenbaum et. al. [2]

The results obtained are presented in the Table below:

Disc Porosity	t_{Cl^-}
2 ("medium")	0.347, 0.347, 0.359, 0.379, 0.362, 0.353, 0.391, 0.36
3 ("fine")	0.380, 0.378, 0.382
4 ("very fine")	0.389, 0.354, 0.355, 0.379, 0.386, 0.348

Mean value of t_{Cl^-} = 0.368 ± 0.014

Maximum deviations from mean value + 0.023, - 0.021.

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1. Boardman, Dorman & Heymann, J. Physic. Chem., 53, 375 (1949)
2. Kirshenbaum, Cahill and Grosse, J. Inorg. Nucl. Chem., 22, 33 (1961)

Accuracy of Experimental Data

The major source of inaccuracy in the experiments was the uncertainty in the measurement of volume changes due to electrolysis. The travelling microscope used could be read to within $\pm$ 0.0005 cm., and the smallest salt / air interface displacements were of the order 0.005 cm., thus giving rise to errors, in this case, of the order $\pm$10% The largest observed displacements, on the other hand, were about 0.13 cm. The error in such cases as the latter was thus of the order $\pm$ 0.5%. Hence the mean probable error in Δ V would have been about $\pm$ 5%.

Another possible source of error was the measurement of capillary radii. The reproducibility of these determinations was within $\pm$ 0.5%. The expansion of the Pyrex capillaries between room temperature and 550^{o}C introduces negligible error.

Allowing for small uncertainties in V_{MX_2} and V_M, and in the temperature of the electrolyte, the experimental results are probably accurate within approximately $\pm$ 6%

The mean value obtained for the anion transport number, t_{Cl^-} , is therefore to be expressed as

$$t_{Cl^-} = 0.37 \pm 0.01$$

D. Discussion

The mean value obtained for the anion transport number in fused lead chloride, from eighteen separate determinations, namely

$$t_{Cl^-} = 0.37 \pm 0.01$$

at 550°C, is in good agreement with the results of Bloom and Doull [1] (i.e. 0.39 ± 0.01). The present value, however, is in poor agreement with the results of Karpachev and Pal'guev [2] (0.78), Delimarskii, Turov and Gitman [3] (0.83), Duke and Laity [4] (0.78) and Duke and Cook [5] (0.76), all at approximately 550°C. The criticism by Lorenz and Janz [6] of Bloom and Doull's measurements is, in the present author's opinion, invalid, and in any case the present technique precludes any possibility of error associated with the movement of the liquid lead in the cell capillaries. Of the other Hittorf-type measurements, those of Duke and Laity are probably the least inaccurate; however, as discussed previously (see Introduction) Duke and Laity's results almost certainly have very large errors associated with them.

Duke and Cook's value for t_{Cl^-} in $PbCl_2$ was measured by a moving-boundary method. While their method was not

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1. Bloom and Doull, J.Physic.Chem., 60, 620 (1956)
2. Karpachev and Pal'guev, Zh.Fiz.Khim., 23, 942 (1949)
3. Delimarskii, Turov and Gitman, Ukrain.Khim.Zh., 21, 314 (1955)
4. Duke and Laity, J.Amer.Chem.Soc., 76, 4046 (1954)
5. Duke and Cook, J.Physic.Chem., 62, 1593 (1958)
6. Lorenz and Janz, J.Physic.Chem., 61, 1683 (1957)

particularly accurate ($t_{Cl^-} = 0.76 \pm 0.04$) there are no obvious sources of error sufficiently large to account for the difference between their value of t_{Cl^-} and that obtained in the present work.

The Effect of the Porous Disc

Sinistri[1] has discussed the significance of cationic and anionic transport numbers in a pure fused salt, particularly with regard to the importance of the frame of reference. He has shown that the transport numbers are arbitrary quantities which become defined automatically when the reference frame for velocities is fixed. Sinistri states further, that transport numbers measured by the methods utilising a porous disc involve the system "porous diaphragm - fused salt" and not the pure fused salt. He says "...considerable uncertainties are introduced by such factors as electro-osmosis, glass - salt interactions, etc.... For all these reasons the meaning of transport numbers of the system fused salt - porous diaphragm appears to be rather uncertain." Let us examine Sinistri's statements in detail. The term electro-osmosis is ordinarily used to refer to the flow of liquid through a membrane (or tube) due to the passage of an electric current. In dilute electrolyte solutions it is attributed to the effect of the electric field on the electric double layers of ions, formed at boundary surfaces between membrane and solution. In general, the electro-osmotic effect decreases with ionic strength and hence in the fused salt, with high ionic strength, it is theoretically unlikely that such double layers are formed. If no electric double layers are established then it is not possible for the transport numbers measured in a cell containing a porous diaphragm to be influenced by electro-

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1. Sinistri, J.Physic.Chem., 66, 1600 (1962)

osmotic effects. If significant electro-osmotic effects were operative in the system, then they would be manifest as a systematic variation in observed transport number with diaphragm porosity and electrolysis current. They would, furthermore, depend on the nature of the material of the diaphragm. The observed transport numbers would be functionally dependent on current, because formation of electric double layers would be inhibited to a greater and greater extent with increasing current. The fact that the transport numbers observed in this work were quite independent, within experimental error, of diaphragm porosity and electrolysis current indicates that if electro-osmotic affects were present then they were negligibly small and, therefore, introduced no sensible uncertainty into the measured values of transport number.

In contrast to Sinistri's conclusions [1], experiments have been reported which show that the results of transport number measurement in porous diaphragm - salt systems are not changed by substituting quartz, alundum or similar materials for glass, in the porous diaphragm (e.g. Duke and Laity [2]). This observation implies that, although there may be a transfer of momentum between the porous diaphragm and the molten salt, such a momentu transfer is a phenomenon of the salt alone and is not due to "glass - salt interactions" specific to various materials.

There is considerable experimental evidence to

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1. Sinistri, J.Physic Chem., 66, 1600 (1962)
2. Duke and Laity, J.Physic Chem., 59, 549 (1955)

indicate, therefore, that Sinistri's criticisms of the porous diaphragm techniques are unfounded.

It is possible that forces exerted between salt and cell arise from surface effects along the boundary between salt and cell. If so, the measured values of transport number would be sensitive to the geometry of the cell. In fact, a study of the different sizes and shapes of cells which have been used by various workers, indicates that the geometry of the cell is not a critical factor, and hence surface effects at the cell / salt boundary evidently do not affect the measurements significantly.

The Frame of Reference

As pointed out by Sinistri[1], the transport numbers for a pure fused salt become automatically defined when the reference frame for velocities has been fixed. In theory, but not in practice, it is possible to assign an internal reference frame with respect to which ionic velocities and transport numbers may be defined. Such a reference frame might be the centre of mass of the salt, for example, or the centre of volume. Within such a frame, the "inner" transport numbers (after Klemm[2]) are perfectly well defined. A natural choice of external frame of reference is the porous diaphragm, and thence the "outer" transport numbers (Klemm[2]) are consistently defined. Klemm has devised a theoretical treatment of transport in molten salts[2] and has calculated theoretical "outer" transport numbers for $PbCl_2$; his value for t_{Cl^-} is in good agreement with the value observed in the present work.

Klemm has discussed[3] in detail, "outer" transport numbers defined with respect to the walls of the cell. He considers measurements (of external mobilities) performed in an electrolytic cell, containing a diaphragm with pore size sufficiently small to prevent uncontrolled diffusion, but sufficiently large to justify neglecting ionic transport within a distance, l, of the wall. l is a critical length representing the distance from the wall in which the mobilities vary. A rather similar treatment has been given

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1. Sinistri, J.Physic Chem., 66, 1600, (1962)
2. Klemm, Z.Naturforsch., 15a, 173, (1960)
3. Klemm, in "Molten Salt Chemistry", editor Blander, 8th Chapter, Interscience U.S.A. (1964)

by Sundheim[1], who notes that viscosity studies have indicated that molten salts display Newtonian flow in viscometer capillaries. This implies that the salts, which, in general, wet the construction materials, meet laminar boundary conditions; i.e. the velocity of flow tends to zero as the wall is approached. It is assumed that when two kinds of ions are moving in different directions under the influence of the electric field, the ionic velocities individually tend to zero at the wall. The transition between zero velocity at the wall and the velocity observed from the wall, is presumed to take place in a boundary layer of unknown, but presumably very small, dimensions.

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1. Sundheim, in "Fused Salts", editor Sundheim, Chapter 3, McGraw-Hill, U.S.A. (1964)

An Examination of Structural Models and Transport Mechanisms

A number of models have been proposed to describe ionic migration in fused salts. Sundheim[1], in his treatment of transport of electrolyte through a porous diaphragm, used the basic hypothesis that a porous diaphragm will assume the mass-average velocity of the ions flowing through it. He assumed that no momentum is transferred between the salt and the transport cell, and concluded that the transport numbers of anion and cation in a simple molten salt should be given by the relationships

$$t_+ = \frac{M_-}{M_+ + M_-} \qquad \ldots(1a)$$

$$t_- = \frac{M_+}{M_+ + M_-} \qquad \ldots(1b)$$

where M_+ and M_- are the formula weights of cation and anion respectively, t_+ and t_- their transport numbers. The view that no momentum is transferred to the cell appears to represent a highly idealised situation, unattainable in practice. The implicit assumption is made that the liquid move freely along the walls of the container. However, even when there is no preferential absorption of one ion with respect to another, there could still be frictional interaction between ions of similar type, one being held to the surface while the other tends to move. Beshers[2] has concluded that Sundheim's model corresponds to a totally ionised perfect gas, with no constraints at the electrodes. Clearly this model should not be applicable

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1. Sundheim, J.Physic Chem., 60, 1381 (1956)
2. Beshers, quoted in "Modern Aspects of Electrochemistry", No.2, editor Bockris, Butterworths, London (1959)

to molten electrolytes. In practice, the transport numbers for $PbCl_2$ predicted by this model do not agree with any of the values which have been obtained experimentally. Moreover, for molten salts in general, the transport numbers are not in accord with this model.

Frenkel [1] has suggested that only one of the ions in a molten salt should be responsible for the electrical conduction, namely the smaller ion. On the basis of this model, the cation should in general have transport number unity, because it (generally) has the smaller radius. This is not in agreement with experimental data.

Mulcahy and Heymann [2] compared the conductances of alkali halides at a corresponding temperature ($\frac{3}{4}$ of the boiling point). They found that their data obeyed the relationship

$$\Lambda = k\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad \ldots(2)$$

where r_+ and r_- are the radii of anion and cation respectively. From this observation it was deduced that in the alkali halides the transport numbers should be given by the equations

$$t_+ = \frac{r_-}{r_+ + r_-} \qquad \ldots(3a)$$

$$t_- = \frac{r_+}{r_+ + r_-} \qquad \ldots(3b)$$

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1. Frenkel, "The Kinetic Theory of Liquids", Oxford, London (1946)
2. Mulcahy and Heymann, J.Physic.Chem., 47, 485 (1943)

Transport numbers, calculated from these equations for a large number of uni-univalent salts, are in close agreement with experimental values[1,2].

1. Duke and Owens, J. Electrochem.Soc., 105, 548 (1958)
2. Duke & Bowman, ibid., 106, 626 (1959)

CHAPTER 3

Concentration Cells with Transference, with Molten Salt Electrolytes

A. INTRODUCTION

Consider the electrochemical cell

$$M \;\underset{E_1}{|}\; MX_2 + M^1X_{x_{(i)}}^{(i)} \;\underset{E_3}{\|}\; MX_2 + M^1X_{x_{(ii)}}^{(ii)} \;\underset{E_2}{|}\; M \qquad \ldots I$$

M is a divalent metal, M^1 a monovalent metal, X a halogen; $MX_2 + M^1X$ is a molten mixture of the two pure salts MX_2 and M^1X. The numbers (i) and (ii) refer to the electrolytes in the two half-cells, and $x_{(i)}$ and $x_{(ii)}$ are the mole fractions of MX_2 in the two electrolytes. The numbers 1, 2 and 3 refer to the three phase boundaries of the cell, and symbols E_1, E_2 and E_3 are the electric potential differences across the respective phase boundaries.

Assume that the only species present in electrolytes (i) and (ii) are M^{2+}, M^+ and X^- ions. Further, let us apply the following restraints to the phase boundaries: boundaries 1 and 2 are permeable only to M^{2+} ions and to electrons (i.e. the two electrodes (M) are reversible with respect to M^{2+} ions) and boundary 3 is permeable to M^{2+}, M^+ and X^- ions. The overall cell reaction is the transfer of MX_2 from the electrolyte in which the concentration of MX_2 is the greater to the electrolyte in which the concentration of MX_2 is the lesser. In cell I, let $x_{(i)} > x_{(ii)}$. Then the cell reaction is the transfer of MX_2 from electrolyte (i) to electrolyte (ii).

The cell E.M.F., E_t, is given by the relationship

$$E_t = E_1 + E_2 + E_3 . \qquad \ldots(i)$$

E_1 and E_2 are the electrode potentials developed at the two electrodes and E_3 is the "diffusion potential" (or "liquid-junction potential"). If $a_{(i)}$ and $a_{(ii)}$ are the thermodynamic activities of MX_2 in electrolytes (i) and (ii), and if E_3 be denoted by ϵ, then the cell E.M.F. is given by the relationship

$$E_t = -\frac{RT}{nF} \ln \frac{a_{(ii)}}{a_{(i)}} + \epsilon \qquad \ldots(ii)$$

where R is the gas constant, T the absolute temperature, F is the Faraday and n the valency of the ion with respect to which the electrodes are reversible. In the present work, cells analogous to cell I, of the type

$$Pb \mid PbX_2 + MX \,\|\, PbX_2 + MX \mid Pb \qquad \ldots II$$
$$x_{(i)} \qquad\qquad x_{(ii)}$$

(where X = Cl, Br; M = Na, K, Rb, Cs) were set up and their E.M.F's measured, $x_{(i)}$ varying between 1.0 (pure PbX_2) and 0.5 (approximately). The liquid junction (phase boundary 3) was established by separating the two half-cells by a porous silica disc.

Consider now the concentration cell without transference, corresponding to cell I :

$$M \overset{1}{\mid} MX_2 + M^1X \overset{3}{\|} MX_2 + M^1X \overset{2}{\mid} M \qquad \ldots(III)$$
$$x_{(i)}^{(i)} \qquad\qquad x_{(ii)}^{(ii)}$$

Phase boundary 3 is now impermeable (no transference of electrolyte takes place and the cell cannot be set up experimentally in this form. A cell equivalent to cell III is constituted, however, by the combination of two cells of the type

$$M \mid MX_2 + M^1X \mid X_2 \quad (1 \text{ atmosphere pressure}) \qquad \ldots(IVa)$$
$$x_{(i)}$$

$$M \mid MX_2 \underset{x(ii)}{} + M^1X \mid X_2 \quad (1 \text{ atmosphere pressure}) \qquad \ldots(IVb)$$

If cells IVa and IVb be connected back to back then we have the cell:

$$M \mid MX_2 \underset{x(i)}{} + M^1X \mid X_2 \quad (1 \text{ atm.}), X_2 \ (1 \text{ atm.}) \mid MX_2 \underset{x(ii)}{} + M^1X \mid M \quad \ldots(V)$$

which is identical to cell III. Assume that $x_{(i)} > x_{(ii)}$. The E.M.F. of the concentration cell without transference (cell III) can thus be deduced by measuring the E.M.F's of corresponding formation (or "chemical") cells (IVa and IVb) and subtracting the latter. The E.M.F. of the cell without transference, E, is given in principle by the relationship

$$E = -\frac{RT}{nF} \ln \frac{a(ii)}{a(i)} \qquad \ldots (iii)$$

where the symbols have the same significance as before (equation (ii), above).

Hence, the value of the diffusion potential, $\mathcal{E}$, may be calculated from the difference in E.M.F's of cells I and III, i.e. comparing equations (ii) and (iii) :

$$\mathcal{E} = E_t - E \qquad \ldots(iv)$$

This is the only known procedure, to the author's knowledge, for the determination of diffusion potentials. In principle, it does not seem possible to measure this quantity directly because in order to measure E_3 of cell I it would be necessary to use a procedure such that the magnitude of E_3 were measured specifically, apart from E_1 and E_2. There is no simple manner in which this may be done without affecting the cell as a whole. In effect, some form of "inert" measuring electrodes would be necessary, which did not interact

with the cell in any way. However, the two "inert" electrodes would have to be in electrical contact with electrolytes (i) and (ii), and such electrical contact would necessarily give rise to electrode potentials at the corresponding phase boundaries, thus invalidating the measurement.

In the present work, values of the diffusion potentials in various molten salt systems, for differing compositions and at several temperatures, were obtained by the indirect method discussed above. The values of the E.M.F's of the cells without transport were obtained from the work of Lantratov and Shevlyakova [1], Markov, Delimarskii and Panchenko [2] and White [3].

The diffusion potential arises as a consequence of thermodynamically irreversible diffusion processes taking place at the liquid junction. These diffusive processes must be governed by, inter alia, the nature and relative concentration of the ionic and/or molecular species of which the molten electrolytes are composed. The explicit "structural dependence" and temperature dependence of the diffusion potential has been hitherto unknown and, in fact, the concept itself has not been intensively investigated either theoretically or experimentally. It was felt, therefore, that a thorough investigation of diffusion potentials in molten salt systems could shed valuable light both on the magnitude and physical significance of this property, and also on the microscopic constitution of the molten electrolytes themselves.

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1. Lantratov and Shevlyakova, Zh. Neorgan.Khim., 6, 95 (1961)
2. Markov, Delimarskii and Panchenko, Zh.Fiz.Khim., 28, 1987 (1954)
3. White, to be published.

Review of Previous Work on Concentration Cells with Molten Salt Electrolytes.

Early work [1-7] on cells with molten salt electrolytes was directed toward comparison of the heats of formation, of metallic chlorides, from E.M.F's of cells with those values obtained by calorimetric methods. Concentration cells of the type

$$Pb \mid PbCl_2 \,\|\, Sn\,Cl_2 \mid Sn \qquad \ldots V$$

were investigated to determine the difference in the free energies of formation of the two molten salts. The magnitude of the diffusion potential was shown to be small where the salts were similar in nature, e.g. $SnCl_2$ - $PbCl_2$, $CdCl_2$ - $PbCl_2$. Predictions of the E.M.F's of cells

$$M^1 \mid M^1Cl_2 \,\|\, M^{11}\,Cl_2 \mid M^{11} \qquad \ldots VI$$

(where M^1 and M^{11} are heavy metals) were made from the E.M.F's of cells of the type

$$M^1 \mid M^1\,Cl_2 \mid Cl_2 - Cl_2 \mid M^{11}\,Cl_2 \mid M^{11} \qquad \ldots VII$$

This work involved, in effect, measurement of diffusion potentials. The cell

$$Ag \mid AgCl \,\|\, PbCl_2 \mid Pb \qquad \ldots VIII$$

was investigated by Suchy [8], while the cell

$$Cd \mid CdCl_2 \,\|\, PbCl_2 \mid Pb \qquad \ldots IX$$

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1. Czapinski, Z.Anorg.Chem., 19, 208 (1899)
2. Webber, Z.Anorg.Chem., 21, 305 (1899)
3. Lorenz and Fox, Z.physik.Chem., 63, 109 (1908)
4. Lorenz, Z.physik.Chem., 130, 39 (1927)
5. Lorenz and Oppenheimer, Z.anorg.Chem., 161, 183 (1927)
6. Lorenz and Michael, Z.physik.Chem., 137, 1 (1928)
7. Lorenz and Welde, Z.anorg.Chem., 183, 81 (1929)
8. Suchy, Z.anorg.Chem., 27, 152 (1901)

was studied by Holub, Neubert and Sauerwald [1].

Little of the early work was sufficiently precise to allow a contribution to knowledge of molten salts to be made from it.

Pletenev and Rosov [2] measured the E.M.F's (at only one temperature) of concentration cells containing such media as molten KCl + LiCl, $CaCl_2$ + NaCl and KCl + $MgCl_2$ eutectics, as solvents. A cell typical of those studied was

$$Ag \mid AgCl \,\|\, AgCl \quad (KCl + MgCl_2) \mid Ag \qquad \ldots X$$

The assumption which was made, that such media as KCl + $MgCl_2$ are indifferent in that they do not influence the magnitude of the cell E.M.F., is undoubtedly false. Pletenev and Rosov deduced that complex ions are formed in the molten salt wherever the phase diagram of the metal salt (e.g. AgCl) plus one of the component salts, indicated compound formation. The quantitative conclusions of these workers are probably not justified by the accuracy of their measurements.

Ellingham and co-workers [3] studied the thermodynamics of metal reduction processes, by measuring the E.M.F's of Daniell type (concentration) cells. The cells investigated were

$$Pb \mid PbCl_2 \,\|\, AgCl \mid Ag \qquad \ldots XI$$

$$Pb \mid PbCl_2 \,\|\, AgCl \mid AgI \mid Ag \qquad \ldots XII$$

$$Sn \mid SnCl_2 \,\|\, AgCl \mid Ag \qquad \ldots XIII$$

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1. Holub, Neubert and Sauerwald, Z.physik.Chem. 174, 161 (1935)
2. Pletenev and Rosov, Acta Physicochem. URSS, 7, 339 (1937)
3. Rose, Davis and Ellingham, Disc.Faraday Soc. 4, 154 (1948)

$$Sn \mid SnCl_2 \,\|\, AgCl \mid AgI \mid Ag \qquad \ldots XIV$$

$$Pb \mid PbCl_2 \,\|\, SnCl_2 \mid Sn \qquad \ldots XV$$

$$Ag \mid AgI \,\|\, AgCl \mid Ag \qquad \ldots XVI$$

The results of these measurements showed that the combinations (XI - XIII) and (XII - XIV) had E.M.F's different from that of cell XV, implying that the diffusion potentials across the junction $SnCl_2 \,\|\, PbCl_2$ is considerably different from those across the junctions $AgCl \,\|\, PbCl_2$ and $AgCl \,\|\, SnCl_2$. These workers suggested that the difference in diffusion potential was due to a specific interaction of AgCl with $PbCl_2$ and $SnCl_2$. There is evidence which indicates that this conclusion is false.[1] The difference is due, in fact, to the differences between the mobilities of the various cations in the system (e.g. Sn^{2+}, Pb^{2+}, Ag^{+}); the reasons for the unequal mobilities are not obvious.

A concentration cell with two oxygen electrodes was studied by Flood et al.[2]:

$$(Pt)\ CO_2,\ O_2 \mid (Na_2CO_3,\ Na_2SO_4)_{(i)} \,\|\, (Na_2CO_3,\ Na_2SO_4)_{(ii)} \mid O_2,\ CO_2\ (Pt) \qquad \ldots XVII$$

The liquid junction between the two electrolytes consisted of a magnesium oxide bridge soaked with the electrolyte. The E.M.F. of the cell, as a function of the ionic fraction (x) of carbonate, was found to fit the equation

$$E = \frac{RT}{2F} \ln \frac{x_{(ii)}}{x_{(i)}} \qquad \ldots (V)$$

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1. Salstrom, J.Amer.Chem.Soc., 54, 2653 (1932); 56, 1272 (1934)
2. Flood, Førland and Motzfeldt, Acta Chem. Scand., 6, 257 (1952)

indicating that the carbonate-sulphate system is ideal and that the diffusion potential is negligibly small.

A large number of systems of the type metal / metal ion (in molten salt electrolytes) have been studied. Grjotheim [1], for example investigated concentration cells with electrodes of the metals Cu, Fe, Co, Ni, Cr, Mn and Al in conjunction with electrolytes composed of the metal florides dissolved in large excesses of the NaF - KF mixture. E.M.F. measurements with suitable concentration cells, are in general superior to many other methods of investigation of metal / metal salt systems, as far as elucidation of the chemical reactions involved is concerned, in that a property of the solute can be determined directly i.e., the number of electrons relating the metal to its reaction product(s) in the melt. General treatment of the E.M.F. data has been considered by Crawford [2], Corbett and Albers [3] and Topol et al. [4, 5]. The wider application of this method of investigation is limited by the unavailability of suitable insulating materials stable to some melts, the requirement of a closed cell (for work with volatile components) and the occurrence of electronic conduction in certain molten salt solutions.

The initial application of the concentration cell method to metal / metal salt systems was the investigation of lithium, cadmium and

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1. Grjotheim, Z.physik.Chem., 11, 150 (1957)
2. Crawford, Ph.D. Thesis, London (1960)
3. Corbett and Albers, J.Amer.Chem.Soc., 82, 533 (1960)
4. Topol, Yosim and Osteryoung, J.Physic.Chem., 65, 1511 (1960)
5. Topol and Osteryoung, J.Physic.Chem., 66, 1587 (1962)

lead chlorides (melts) by Karpachev et al. [1-3]. The system Cd - $CdCl_2$ has also been studied by Crawford [4], while the method has been applied to the systems Sb - SbI_3 [5] and Bi - $BiCl_3$ [6]. The study by Topol et al. [7], particularly, on the Bi - $BiCl_3$ system, has yielded information relating to the nature of the species present in this melt. Topol [8] has recently studied cells of the type

$$C, M (N1), MX_2 (1 - N1) \parallel MX_2 (1 - N_2), M (N_2), C \quad \ldots XVII$$

where M represents Hg, Cd, Pb and Zn, and MX_2 the corresponding halide.

Activity coefficients in the system $AgNO_3$ - KNO_3 have been determined by Laity [9] using concentration cells with transference. Laity derived an expression relating the E.M.F., of such a concentration cell containing fused salt electrolytes, to the activities of the salts present, the temperature, and the mobilities of the ions. The thermodynamic analysis revealed that for solutions having the transport properties of the $AgNO_3$ - KNO_3 system, the diffusion potential terms vanish from the E.M.F. expression. The E.M.F. determinations showed that these solutions deviate considerably from thermodynamic ideality, but conform well to the requirements for a "regular solution". Determination of activities in molten salt systems from measuremen of concentration cell E.M.F's depends on knowledge of the magnitude of the

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1. Karpachev and Stromberg, Zh.Fiz.Khim., 13, 397 (1939)
2. Karpachev and Jordan, Zh.Fiz.Khim., 14, 1495 (1940)
3. Karpachev, Stromberg and Jordan, Zh.Fiz.Khim., 18, 43 (1944)
4. Crawford, Ph.D. Thesis, London (1960)
5. Corbett and Albers, J.Amer.Chem.Soc , 82 , 533 (1960)
6. Corbett, Albers and Sallach, unpublished work (1960)
7. Topol, Yosim and Osteryoung, J.Physic Chem., 65, 1511 (1960)
8. Topol, J.Physic.Chem., 67, 2222 (1963)
9. Laity, J.Amer.Chem.Soc., 79, 1849 (1957)

diffusion potentials. Many examples of concentration cells (including Daniell cells), in which the diffusion potential is negligibly small, exist in the literature. Such cells are those containing, for example : $AgNO_3$ in $NaNO_3$ - KNO_3 [1-2], in $NaNO_3$ [3] and in KNO_3 [4-5]; AgCl, $CoCl_2$, $PbCl_2$, $ZnCl_2$, $NiCl_2$, $CdCl_2$, TlCl, CuCl, $CrCl_3$, $MnCl_2$, $FeCl_2$ and $SnCl_2$ in NaCl - KCl mixtures;[6-7] $PtCl_2$, $PdCl_2$, $BiCl_3$, AgCl, $NiCl_2$, CuCl, $PbCl_2$, $FeCl_2$, $CdCl_2$ and TlCl in LiCl - KCl mixtures; [8] KCl in $LiNO_3$ - KNO_3 [9], and KBr and KI in KNO_3 and in KNO_3 - $NaNO_3$ mixtures [10]. Murgulescu and Marchidan [11,12] have investigated diffusion potentials in several systems, including AgCl - KCl, AgBr - KBr, AgBr - NaBr, AgBr - LiBr and AgBr - $PbBr_2$ [12]; 60% KCl - $PbCl_2$ and 20% KCl - $PbCl_2$ [11]; they have found the diffusion potentials to be less than 1 milli volt in all these cases. Murgulescu and Sternberg have pointed out [13] the apparent generality of the

1. Flengas and Rideal, Proc.Roy.Soc.(London) A233, 443 (1956)
2. Gordan, Z.Physik.Chem., 28, 302 (1899)
3. Hill, Braunstein and Blander, J.Physic Chem., 64, 1038 (1960)
4. Blander, Blankenship and Newton, J.Physic.Chem., 13, 1259 (1959)
5. Laity, J.Amer.Chem.Soc., 79, 1849 (1957)
6. Flengas and Ingraham, Can.J.Chem., 35, 1139 , 1254 (1957);36, 780, 1103, 1662 (1958)
7. Flengas and Ingraham; J.Electro.Chem.Soc., 106, 714 (1959)
8. Laitinen and Liu, J.Amer.Chem.Soc., 80, 1015 (1958)
9. Bonnemay and Prideaux, Compt.Rend., 240, 1774 (1955)
10. Braunstein and Lindgren, J.Amer.Chem.Soc., 84, 1534 (1962)
11. Murgulescu and Marchidan, Acad.rep.populare Romine, Studii Cercertari Chim, 5 , 383 (1960)
12. Murgulescu and Marchidan, ibid, 7 , 461 (1963)
13. Murgulescu and Sternberg, Disc.Faraday Soc., 32, 107 (1961)

near equality of cation mobilities (and hence zero diffusion potentials) in many binary systems. Laity and Moynihan[1] have reviewed the available data and summarised it as follows: "...data reported for at least ten different systems are consistent with the hypothesis that the mobilities of like-charged ions in fused salt mixtures are equal within about 10 - 15% at all concentrations. If the moving - boundary results (Klemm and Monse[2]) for $PbCl_2$ - LiCl are valid, the latter system constitutes the only clearcut counter example to this generalisation we have found in the literature." In fact, the results of Duke and Fleming[3], whose data predict a diffusion potential of about 11 millivolts for 60% KCl - $PbCl_2$ and 40% KCl - $PbCl_2$, are also in contrast to this generalisation, as are the results of the present investigation (see Results).

The formation of complex ions in molten salts has been studied by Duke and Garfinkel[4], utilising concentration cells. Thus, these workers followed the formation of bromo-complexes of lead and cadmium by measuring the E.M.F. of an appropriate concentration cell as a function of the concentration of the metal ion employed. They also determined the formation constants of the species Ag^+ Cl^- and $AgCl_2^-$ (in $NaNO_3$ - KNO_3).

To the author's knowledge, almost no systematic investigations of diffusion potentials have previously been conducted in molten salt systems, in respect of the variation of diffusion potential with temperature and composition of the electrolyte. The only work which has hitherto been carried out along these lines appears to be that of Richards.[5]

1. Laity and Moynihan, J.Physic.Chem., 67, 723 (1963)
2. Klemm and Monse, Z.Naturforsch., 12a, 319 (1957)

(continued overleaf)

3. Duke and Fleming, J.Electrochem.Soc., 106, 130 (1959)
4. Duke and Garfinkel, J.Physic.Chem., 65, 461, 1627, 1629 (1961)
5. Bloom and Richards, to be published; Richards, Ph.D.Thesis, University of New Zealand (1956)

B. EXPERIMENTAL

1. Apparatus

(a) Furnace

The electric resistance furnace had a tubular silica block, 1½" inside diameter and 12" long, wound with Kanthal Al B. & S. 19 gauge resistance wire. The outer surface of the silica tube was spirally grooved, so that the windings were held in place without refractory cement.

The furnace case was constructed from a frame of ¾" x ¾" x ⅛" angle iron, with sides of ¼" thick "Sindanyo" asbestos sheet and was packed with asbestos "wool" lagging. The outside dimensions of the furnace case were 12" x 12" x 15" high. Four angle-iron supports held the furnace 3" above bench-level.

Power was supplied to the furnace via a 1 K.V.A. voltage stabiliser, an Ether "Transitrol" Type 990H temperature controller and a "Variac" variable transformer. The "Transitrol" did not, in practice, control the temperature of the furnace; it was used merely as an approximate temperature indicator, since the experimental procedure used required the furnace to be held at a constant temperature only infrequently (see Experimental Procedure).

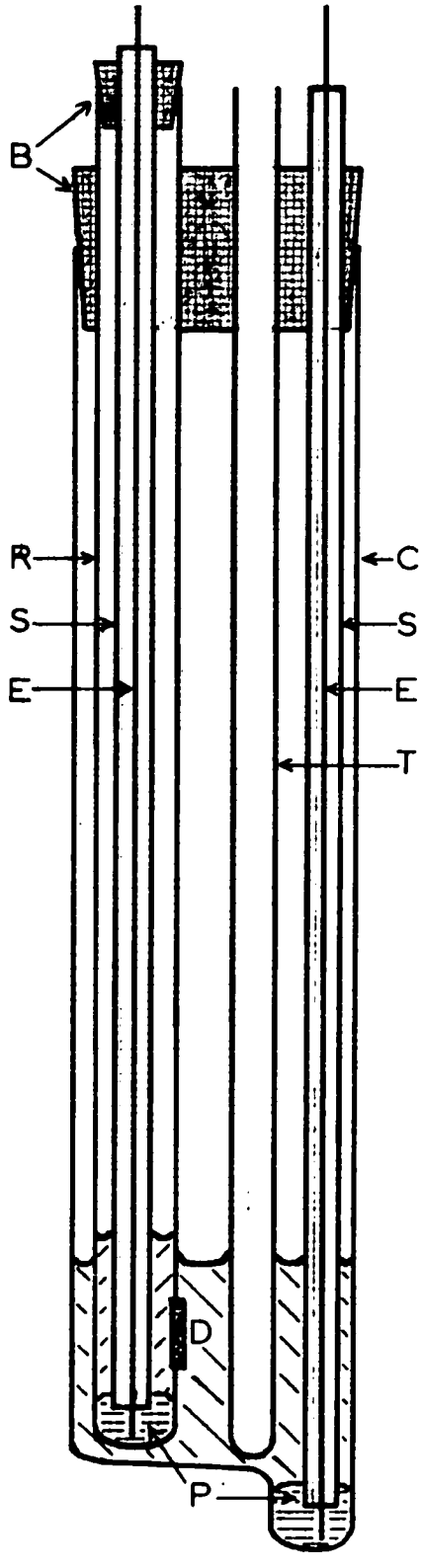
(b) Cell

A diagram of the complete cell is reproduced in Fig. 8 The bulk of the cell was made from transparent "Vitreosil" silica (Thermal Syndicate). The porous discs used were a commercial product of the Thermal Syndicate.

FIGURE 8.

Cell used in diffusion potential measurements.

FIGURE 8



The large container, C (see Fig.8) had length 12", inside diameter 1-1/8" and outside diameter $1\frac{1}{4}$", a protuberance on the lower end being 1/2" in diameter and 1/2" long. The protuberance held a pool of molten lead metal of volume approx. 1 ml. In all cases, that salt mixture which was less rich in lead halide (the "bulk electrolyte") was contained in C.

The "reference" half-cell consisted of a container tube, R, 12" long, 11/32" inside diameter and 13/32" outside diameter. Into the wall of this tube a porous silica disc, D, was sealed. The discs used were nominally "porosity 3" ("fine"), approx. 3/8" in diameter and about 1/16" thick. In the bottom of container R was a pool of molten lead metal of volume approx. 0.5 ml. The centre of the porous disc was located 7/8" above the bottom of R.

Electrical contact with the electrolyte in each half-cell was extablished, via the lead pools, by two electrodes E, whose length was not critical. The electrodes were constructed in the following manner:
A length of 0.016" diameter wire (50% Tungsten, 50% Molybdenum) was sealed into a piece of silica capillary tube, S, of diameter 3/16" and bore 0.03". The seal was accomplished by heating, under vacuum, the lower 3 - 4" of the capillary tube, with the wire in place, thereby collapsing the silica onto the wire. The wire extended approx. 2 - $2\frac{1}{2}$" from the top of the capillary S, and also about 3/16" below the lower end of the capillary in order to make effective contact with the molten lead. At their upper extremity the two electrode wires passed into a double brass connecting block, which was clamped in position above the furnace. The two junctions were situated very close together, so that they were always at equal temperatures and hence

no differential thermo-electric E.M.F. could arise and thereby introduce error into the measurement of cell E.M.F. From the connecting block two copper wires led to a potentiometer.

A thermocouple was contained in the silica sheath T, which had inside diameter 3/16" , outside diameter $\frac{1}{4}$" and length 12".

The component parts of the cell (other than C) were held in position inside the large container C by means of rubber bungs, B. Container C was held in position in the furnace by a simple clamp. The actual position of the cell in the furnace was such that that part of the cell which contained molten salt electrolyte was situated in the region of highest temperature, this region being at an approximately uniform temperature over a distance of about 3".

(c) Measurement of Cell E.M.F.

Two potentiometers were used to measure the cell E.M.F. For all determinations in which the cell E.M.F. was less than 100 millivolts in magnitude, a Leeds and Northrup 8686 Millivolt Potentiometer was employed; this instrument had a range of 0 - 100 millivolts (mv.). For those experiments in which the cell E.M.F. was greater than 100 mv. a Tinsley 3184 D potentiometer was used, since its range was much wider than that of the Leeds and Northrup instrument. The Leeds and Northrup potentiometer was preferred, wherever possible, because with it measurements could be made with greater precision than with the Tinsley instrument.

It was important to use a null-method (such as the

potentiometric method) to measure cell E.M.F. in order to minimise the current drawn from the cell.

(d) Temperature Measurement

The temperature of the molten salt electrolyte was measured with a Platinum-Platinum / 13% Rhodium thermocouple, in conjunctio with a Tinsley 3184 D potentiometer. The 26 s.w.g. thermocouple wires were contained in a $12\frac{1}{2}$" x $\frac{1}{8}$" x $\frac{3}{32}$" double-bore alumina insulator. The cold junction was maintained at 0°C. The thermocouple was calibrated at the following thermometric fixed points:

Freezing point of (A.R.) cadmium	320.9°C
Freezing point of (A.R.) zinc	419.5°C
Freezing point of (electrolytically pure) silver	960.5°C
Freezing point of (A.R.) sodium chloride	800.1°C

2. Materials Used in the Experiments

All materials used were the purest commercially available, or were made from the purest available starting materials. The purities quoted are as specified by the manufacturers. The various manufacturers' names are appreviated as follows:

Hopkin and Williams Ltd.	H & W
British Drug Houses Ltd.	B.D.H.
May and Baker Ltd.	M & B
L.Light and Co. Ltd.	Light
New metals and chemicals Ltd.	N.M. & C
By-products and Chemicals Pty.Ltd.	B.P. & C.
Ajax Chemical Pty.Ltd.	Ajax

The following alkali halides were used:

RbCl - N.M. & C, more than 99.7% pure

CsCl - N.M. & C, more than 99.5% pure; Light, not less than 99.9% pu

NaBr - B.D.H. "Laboratory Reagent", not less than 99% pure

KBr - M & B, "Analar" grade

RbBr - N.M. & C, 99.7% pure

CsBr - N.M. & C, "pure"

All the salts above were used without further purification.

For the generation of HCl and HBr (see Experimental Procedure) B.D.H. "Laboratory Reagent" grade NH_4Cl and NH_4Br were used, together with Ajax "Analar" H_2SO_4.

Lead metal used was both H & W "Analar" grade Pb foil,

and B.D.H. "Analar" foil. Neither product required further purification.

$PbCl_2$ was prepared as described in Section B of Chapter 2. $PbBr_2$ was prepared by a similar method - except that the salt was not evaporated to dryness in the presence of HBr - from M & B "Analar" grade and B.P. & C "Univar" grade $Pb(NO_3)_2$, by precipitation with M & B "Analar" grade HBr.

Na_2MoO_4 used in analysis of the lead halide / alkali halide mixtures was B.D.H. "Analar" grade material. Ammonium acetate and acetic acid (used in analysis) were both B.P. & C "Univar" grade reagents while the HNO_3 used was Ajax "Analar" grade.

The lead halides and alkali halides were kept in an oven, at a temperature of 120°C, when not in use.

3. Experimental Procedure

(a) Preliminary

The volume of bulk electrolyte used in all experiments was approximately 19 ml. (at 600° C). A sufficient volume of reference electrolyte was used to ensure that the level of salt in the reference half-cell was 2 - 3 mm. higher than the level of the bulk electrolyte. The levels were adjusted in this way in order to minimise flow of salt from the bulk electrolyte into the reference electrolyte, by opposing a hydrostatic head against such flow. This was necessary because the quantity of bulk electrolyte was much greater than the quantity of reference electrolyte, hence much greater relative changes in composition would have resulted from a small amount of salt flowing into the reference electrolyte than from a small amount of salt flowing in the reverse direction.

It was found that the "porosity" of the porous disc was a critical factor. With discs of nominal porosity 1 and 2 ("coarse" and "medium"), composition changes in the reference electrolyte were far too great (of the order 10 and 5 mole % respectively); the cell resistance (measured with an A.C. conductance bridge), with such discs, was of the order 30 - 120 ohms. The use of porosity 4 ("very fine") discs, on the other hand, gave rise to negligibly small composition changes and a cell resistance of 1200 - 2000 ohms, but the cell E.M.F's tended to have values inconsistent with the E.M.F's of cells with discs of porosity 1, 2 and 3 (ca. 300 mv. instead of 50 mv., in one case). In practice it was found

that the use of porosity 3 ("fine") discs led to composition changes of not more than 2 mole % (usually much less) and cell resistances of the order 300 - 500 ohms. The E.M.F's of three cells, containing electrolytes of the same composition but utilising discs of porosities 1, 2 and 3 respectively, were initially equal - the E.M.F. of the same cell with disc of porosity 4 was, however, much greater. Porosity 3 discs were, therefore, used exclusively.

Further, it was found that when the difference in mole fraction of PbX_2 (X = Cl, Br) between reference electrolyte and bulk electrolyte was greater than about 0.5, the composition changes during a run were too great, in cells with porosity 3 discs. Hence, the largest composition difference in any cell was approximately 50 mole % PbX_2 and, in most cases, the composition difference did not exceed approximately 25 mole % PbX_2. Those experiments, in which the change in lead halide content of the reference electrolyte exceeded 2 mole %, were disregarded and repeated.

For each salt mixture investigated, the bulk electrolyte was analysed (see Analysis of Salt Mixtures) both before and after the run, and the reference electrolyte (of known initial composition) analysed after each run.

There were found to be upper limits to the temperatures at which the cell E.M.F's could be accurately measured. In those systems which contained $PbBr_2$, decomposition of the electrolyte, resulting in evolution of bromine, appeared to occur at temperatures above 650 - 700°C,

depending on the particular salts and on the composition of the mixtures. With $PbCl_2$ - alkali chloride systems, there was no apparent decomposition of the melt at temperatures up to about 800°C, but above this temperature the cells behaved haphazardly in respect of their E.M.F's. The E.M.F's changed rapidly and erratically, and did not remain steady at a constant temperature. In this respect, it is noteworthy that Richards [1], in his work on molten $PbCl_2$ - alkali chloride concentration cells, observed a similar phenomenon - he ascribed the behaviour of the cells at temperatures above 800°C to an "asymmetry potential" (see Discussion).

(b) Procedure

Salt mixtures were prepared by weighing out appropriate quantities of the component salts - previously dried at 120°C - and fusing in a silica pot. The molten mixtures were thoroughly stirred in order to ensure complete homogeneity and poured into a preheated silica basin, allowed to cool, then ground. The finely ground salts were kept at 120°C for at least $1\frac{1}{2}$ hours, after which time samples were taken for analysis. A particular salt mixture was generally made up from the previous mixture used, by addition of alkali halide and/or lead halide, as required to give the desired composition.

All cell components were thoroughly dried for at least six hours at 120°C before commencing a run. About 10 gm. of lead metal was put into the protuberance of container C, and that quantity of solid salt,

1. Bloom & Richards, to be published; Richards, Ph.D. Thesis, University of New Zealand (1956)

required to give the desired volume of liquid electrolyte, added. The container C was then clamped in position in the furnace, at a temperature in the region of 400°C, and the furnace heated (5 degrees per minute) to the desired temperature. As soon as the salt melted, dry HCl or HBr - depending on whether the salt mixture contained chlorides or bromides - was bubbled through the liquid. This process served two purposes : (i) any oxychloride or oxybromide present in the melt was converted into $PbCl_2$ or $PbBr_2$ by elimination of H_2O and (ii) the melt was efficiently stirred, thus assuring complete homogeneity. HCl and HBr were prepared by dropping concentrated H_2SO_4 onto NH_4Cl and NH_4Br respectively.

The stream of dry HCl or HBr was continued until the approximate furnace temperature (indicated by the "Transitrol") reached the desired maximum value for the measurements - 800°C for the $PbCl_2$ - alkali chloride systems and 650 - 700°C for the $PbBr_2$ - alkali bromide systems. The HCl / HBr inlet tube was removed at this point and the remaining cell components (except the sheathed W / Mo electrode in the reference half-cell) inserted gradually into container C. The appropriate quantities of lead metal and salt were added to the reference half-cell immediately before container R was positioned inside C (in order to minimise absorption of atmospheric water vapour by the salt). When the salt in the reference half-cell had melted, the sheathed W / Mo electrode was inserted into the reference half-cell to make contact with the lead pool and the W / Mo wires clamped in the connecting block. Finally, the Pt - Pt / 13% Rh thermocouple was inserted

into the thermocouple sheath T.

The power supply to the furnace was now adjusted, by means of the "Variac", to allow the cell to come to thermal equilibrium at the desired temperature. The cell was maintained at this temperature until the cell E.M.F. became invariant. In general, the time taken for the E.M.F. to attain a constant value was very short - of the order 2 - 5 minutes - but occasionally up to 30 minutes was required. This period was probably that required for the porous disc to become saturated with molten salt.

When both E.M.F. and temperature had reached steady values, the furnace was cooled slowly (o.3 - 1 degree C per minute), and the cell E.M.F. measured, with the potentiometer, at temperature intervals which varied between 1 and 8 degrees C.

Measurements of E.M.F. were continued in this manner, until the temperature had fallen to about 500°C in the case of $PbCl_2$ - alkali chloride mixtures and about 400°C for $PbBr_2$ - alkali bromide mixtures, unless either the bulk or reference electrolyte began to solidify before these temperatures were reached. If the salt had not solidified, the cell was dismantled and the reference electrolyte and bulk electrolyte poured into preheated silica basins. If solidification had occurred in one of the half-cells (indicated by a very sharp change in cell E.M.F.) the furnace was rapidly heated until the salt melted, upon which the cell was dismantled and the salts poured out. The cooled salts were ground finely and placed in an oven at 120°C. After at least $1\frac{1}{2}$ hours samples of the bulk electrolyte and reference electrolyte were withdrawn for analysis.

On completion of a run, the cell components were soaked for approximately $1\frac{1}{2}$ - 2 hours in hot, concentrated ammonium acetate solution, in order to dissolve any salt remaining in the various parts of the cell. It had been found previously that the solution of ammonium acetate in water was a particularly good solvent for $PbCl_2$ and $PbBr_2$. After this treatment the cell components were thoroughly washed with hot water, rinsed with distilled water and placed in an oven (at $120^{o}C$).

For each system investigated, measurements of cell E.M.F. were conducted at composition intervals of approximately 5 mole % (in respect of the bulk electrolyte). The usual programme was as follows (MX representing alkali chloride or bromide, and x_{PbX_2} denoting the mole fraction of PbX_2 in the mixture) : 5 runs with the cells

$$Pb \mid PbX_2 \;\|\; PbX_2 + MX \mid Pb,$$

$$\text{pure} \qquad x_{PbX_2} \approx 0.95 - 0.75$$

followed by 5 runs with the cells

$$Pb \mid PbX_2 + MX \;\|\; PbX_2 + MX \mid Pb,$$

$$x_{PbX_2} \approx 0.75 \qquad x_{PbCl_2} \approx 0.70 - 0.50$$

then a varying number of runs with the cells

$$Pb \mid PbX_2 + MX \;\|\; PbX_2 + MX \mid Pb.$$

$$x_{PbX_2} \approx 0.50 \qquad x_{PbX_2} \approx 0.45 -$$

The assumption was made, that the sum of the E.M.F's of cells such as I, II and III below is equal to the E.M.F. of cell 4.

$$Pb \mid PbX_2 \;\|\; PbX_2 + MX \mid Pb$$

pure $\quad x_{PbX_2} = 0.75 \qquad \ldots I$

$$Pb \mid PbX_2 + MX \;\|\; PbX_2 + MX \mid Pb$$

$x_{PbX_2} = 0.75 \qquad x_{PbX_2} = 0.50 \qquad \ldots II$

$$Pb \mid PbX_2 + MX \;\|\; PbX_2 + MX \mid Pb$$

$x_{PbX_2} = 0.50 \qquad x_{PbX_2} = 0.25 \qquad \ldots III$

$$Pb \mid PbX_2 \;\|\; PbX_2 + MX \mid Pb$$

pure $\quad x_{PbX_2} = 0.25 \qquad \ldots IV$

In principle, this assumption is fully justifiable, because the overall concentration difference (in cell 4) is equal to the sum of the partial concentration differences (in cells 1, 2 and 3), and in practice there was no evidence that the "additivity" assumption was invalid. The validity of the assumption could not be effectively tested experimentally because the concentration difference in cell 4, for example, is so great that large composition changes would have occurred in measurement of the E.M.F. of the cell and the measured E.M.F would therefore have been very unreliable. The lower limit to x_{PbX_2} in the bu electrolyte was set principally by the melting point of the mixtures concerned and in part by the large quantities of expensive salts (e.g. RbBr and CsBr) required for mixtures rich in alkali halide. The composition range over which E.M.F. measurements were carried out was, therefore, dependent entirely on the particular composition and system under consideration.

There was one important difference between the exper-

imental procedure used in this work and that used by some of the other workers who have measured the E.M.F's of molten salt concentration cells. Richards [1] (for example) measured the steady E.M.F. at a number of constant temperatures and thus obtained E.M.F. values at temperature intervals of 20 - 30°C. In the present work, the E.M.F. was measured as the temperature continuously varied, except for the initial "equilibrium" condition. It was found that, provided the cell was cooled at a reasonably slow rate, the measured values of E.M.F. were in fact identical, within experimental error, with those values obtained using the "equilibrium" method. This was ascertained by measuring the cell E.M.F. under four different types of thermal conditions:

1. While the temperature increased slowly,
2. While the temperature decreased slowly,
3. At constant temperature,
4. While the temperature decreased rapidly.

All the E.M.F. values measured, in one run, under these four types of conditions, were collinear within experimental error, when plotted against temperature. The only E.M.F. values which deviated from collinearity were those measured while the rate of fall of temperature was relatively very great - of the order 15 degrees C per minute. Thus, the inherent

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1. Bloom and Richards, to be published; Richards, Ph.D. Thesis, University of New Zealand (1956)

assumption that a type of "dynamic equilibrium" obtains, at reasonably low rates of cooling, has been thoroughly justified.

Additional evidence for the validity of this assumption comes from the work of Grube and Rau [1] who used precisely the same kind of dynamic technique, viz. measurement of cell E.M.F. while the cell temperature slowly changed. These workers appear to have been satisfied that no sensible errors were introduced by the procedure.

(c) Analysis of Salt Mixtures

All volumetric equipment used in analysis was calibrated A-grade apparatus (E-MIL, Green Line).

The compositions of the salt mixtures were determined by analysing the mixtures for their lead content. Two variations of fundamentally the same method were employed, because the procedure which was successfully used to analyse $PbCl_2$ - alkali halide mixtures was found to be unsatisfactory for $PbBr_2$ - alkali bromide mixtures.

The principle of the method was the precipitation of lead, from solution, as insoluble lead molybdate, by titrating the lead-containing solution against standardised sodium molybdate solution. Absorption indicators were used to determine the equivalence point in the titrations.

Procedure for Chloride Systems

That weight of salt mixture which contained approximately 0.5 gm. of $PbCl_2$ was dissolved in ca. 20 ml. of boiling, concentrated ammonium acetate solution, to which had been added a

1. Grube and Rau, Z. Elektrochem., 40, 352 (1934)

few drops of glacial acetic acid. The solution was cooled to room temperature then made up to 500 ml., and 25 ml. aliquots of the solution titrated against approximately 0.025N sodium molybdate solution. To each 25 ml. aliquot of lead solution was added 10 drops of glacial acetic acid and 5 drops of diphenyl carbazone indicator (diphenyl carbazone dissolved in 80% ethanol/ 20% water). The sodium molybdate solution was standardised against a standard solution of pure $PbCl_2$.

Procedure for Bromide Systems

The procedure used for chlorides gave inaccurate and quite irreproducible results when applied to the analysis of $PbBr_2$ - alkali bromide mixtures. The procedure used consequently for the bromides was as follows: a sample containing approx. 0.8 gm. $PbBr_2$ was covered (in a 250 ml. conical beaker) with about 10 - 15 ml. of concentrated nitric acid, heated almost to boiling, and an approximately equal volume of water added; the exact quantities of nitric acid and water were not critical. The solution was then carefully evaporated on a hot-plate until the volume of the solution had been reduced to about 10 ml., when approx. 50% of the $Pb(NO_3)_2$ had precipitated from the solution, then evaporated to dryness under an infra-red drying lamp. When dry (i.e. all HCL or HBr, excess HNO_3 and water removed), the $Pb(NO_3)_2$ was dissolved in about 20 ml. of water plus one drop of ca. 3 N HNO_3. The resulting solution was made up to 500 ml.

25 ml. aliquots of this solution were titrated against approx. 0.0125 N sodium molybdate solution, one drop of ca. 3N HNO_3 and 2 drops of Solochrome Red B 125 indicator (Solochrome Red B 125 dissolved in water) being added to each aliquot. For analysis of $PbBr_2$ - alkali bromide mixtures the sodium molybdate solution was standardised against a standard solution of pure lead bromide.

It was necessary to carry out the lead / molybdate titrations under roughly the same conditions of lighting, especially when using diphenyl carbazone indicator, because the colour of the solution at the equivalence point appeared to vary somewhat with the lighting conditions.

The analytical method utilising diphenyl carbazone as indicator was based on the method of Dubrovskaya and Filippova [1], while the procedure with Solochrome Red B 125 was derived from the method of Holness [2].

1. Dubrovskaya & Filippova, Zavodskaya Lab., 21, 523 (1955)
2. Holness, Analyst, 69, 145 (1944)

C. RESULTS

Six salt systems were investigated as molten electrolytes in concentration cells with transference : $PbBr_2$ - CsBr, $PbBr_2$ - RbBr, $PbBr_2$ - KBr, $PbBr_2$ - NaBr; $PbCl_2$ - CsCl and $PbCl_2$ - RbCl. The systems $PbCl_2$ - KCl and $PbCl_2$ - NaCl were not studied because they had been previously investigated by other workers (e.g. Richards[1]), and the lead halide - lithium halide systems were not studied, principally owing to the difficulty in obtaining sufficiently pure lithium salts.

1. Concentration Cell E.M.F's

(i) Temperature Dependence of E.M.F.

In the experiments, the E.M.F's of the concentration cells were measured at small temperature intervals (varying between approx. 1 and 8° C, in general). The measured values of E.M.F. were plotted against temperature, when it was observed that for almost all mixtures, the points $[E_t , T]$ lay, with very small deviation, on a series of straight lines. The lines of best fit were drawn as accurately as could be judged visually. The equations to the lines of best fit were then computed (using the method of least squares), with an appropriate programme (reproduced in Appendix 2), by an Elliott 503 computer. For the computations, points which appeared to lie on a particular linear portion of the experimental E.M.F. / temperature plot were assumed to do so, and the equation to the straight line of best fit for these points computed. This process was repeated for each other

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1. Bloom and Richards, to be published; Richards, Ph.D. Thesis, University of New Zealand (1956)

series of collinear points.

The lines of best fit, plotted from the computed equations are shown in Figures 9 (i) ($PbBr_2$ - CsBr), (ii) ($PbBr_2$ - RbBr), (iii) ($PbBr_2$ - KBr), (iv) and (v) ($PbBr_2$ - NaBr); Figures 10 (i) ($PbCl_2$ - CsCl), (ii) and (iii) ($PbCl_2$ - RbCl). The results obtained are presented in Tables 1, (i) to (iv), and Tables 2, (i) and (ii), below. In these tables, x^1 denotes the mole fraction of PbX_2 (X = Cl or Br) in the reference electrolyte, x the mole fraction of PbX_2 in the bulk electrolyte. T_c denotes the temperatures at which changes in slope appear on the plots; T_c was calculated from the equations to the various lines. The highest and lowest temperatures appended to the E.M.F. / temperature equations are experimental extrema. The units of E are millivolts, and of T, degrees Centigrade.

The experimentally obtained points are not included in the plots, because the deviations of the experimental points from the straight lines are so small that the great majority of the points lie on the computed lines.

For those cases in which E.M.F. was measured with respect to a mixture in the reference half-cell rather than pure lead halide the absolute values of E.M.F. (i.e. with respect to pure lead halide) were calculated by addition of the E.M.F's of the appropriate cells (see Experimental).

FIGURE 9

Plot of E.M.F. of concentration cells with transference against temperature, for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr

(iv) and (v) $PbBr_2$ - NaBr.

FIGURE 9 (i)

The letters a, b, etc. specify the mixtures for which the various plots were obtained. The mole-fractions of $PbBr_2$ in the various mixtures are given by x^R, the mole - fraction of $PbBr_2$ in the reference electrolyte and x^B, the mole-fraction of $PbBr_2$ in the bulk electrolyte.

	x^R	x^B
a	1.00	0.949
b	1.00	0.888
c	1.00	0.845
d	1.00	0.798
e	1.00	0.750
f	0.750	0.700
g	0.750	0.654
h	0.750	0.603
i	0.750	0.550
j	0.750	0.510
k	0.510	0.454
l	0.510	0.408
m	0.510	0.355

FIGURE 9(1)

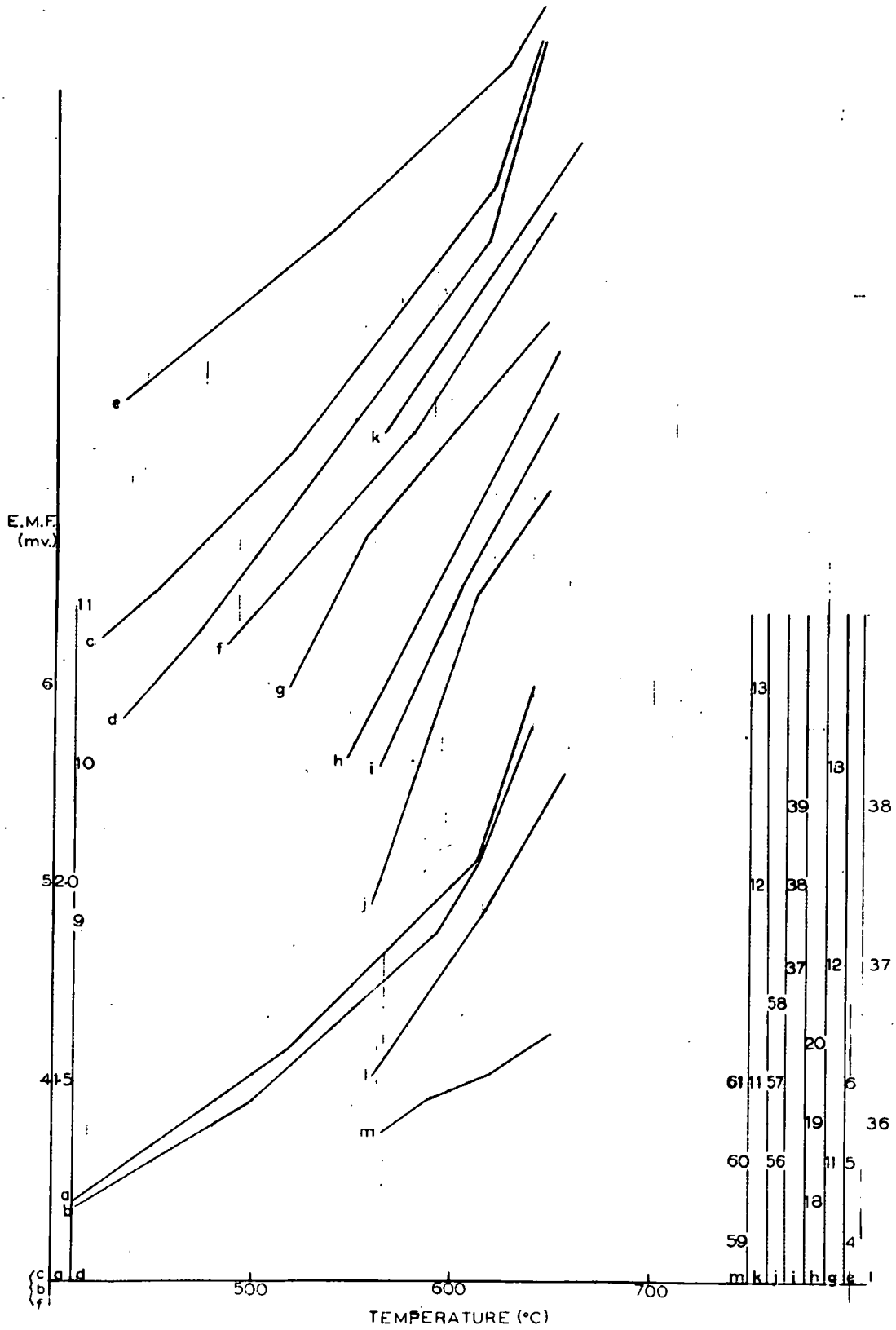

E.M.F.
(mv.)
6
5
4
500
600
700
TEMPERATURE (°C)
a
b
c
d
e
f
g
h
i
j
k
l
m
11
10
9
2·0
1·5
13
12
39
38
37
58
20
61
57
19
60
56
18
59
4

FIGURE 9 (11)

	x^R	x^B
a	1.00	0.942
b	1.00	0.899
c	1.00	0.842
d	1.00	0.800
e	1.00	0.744
f	0.744	0.694
g	0.744	0.646
h	0.744	0.597
i	0.744	0.546
j	0.744	0.500
k	0.500	0.444
l	0.500	0.398
m	0.500	0.348
n	0.500	0.300

FIGURE 9(ii)

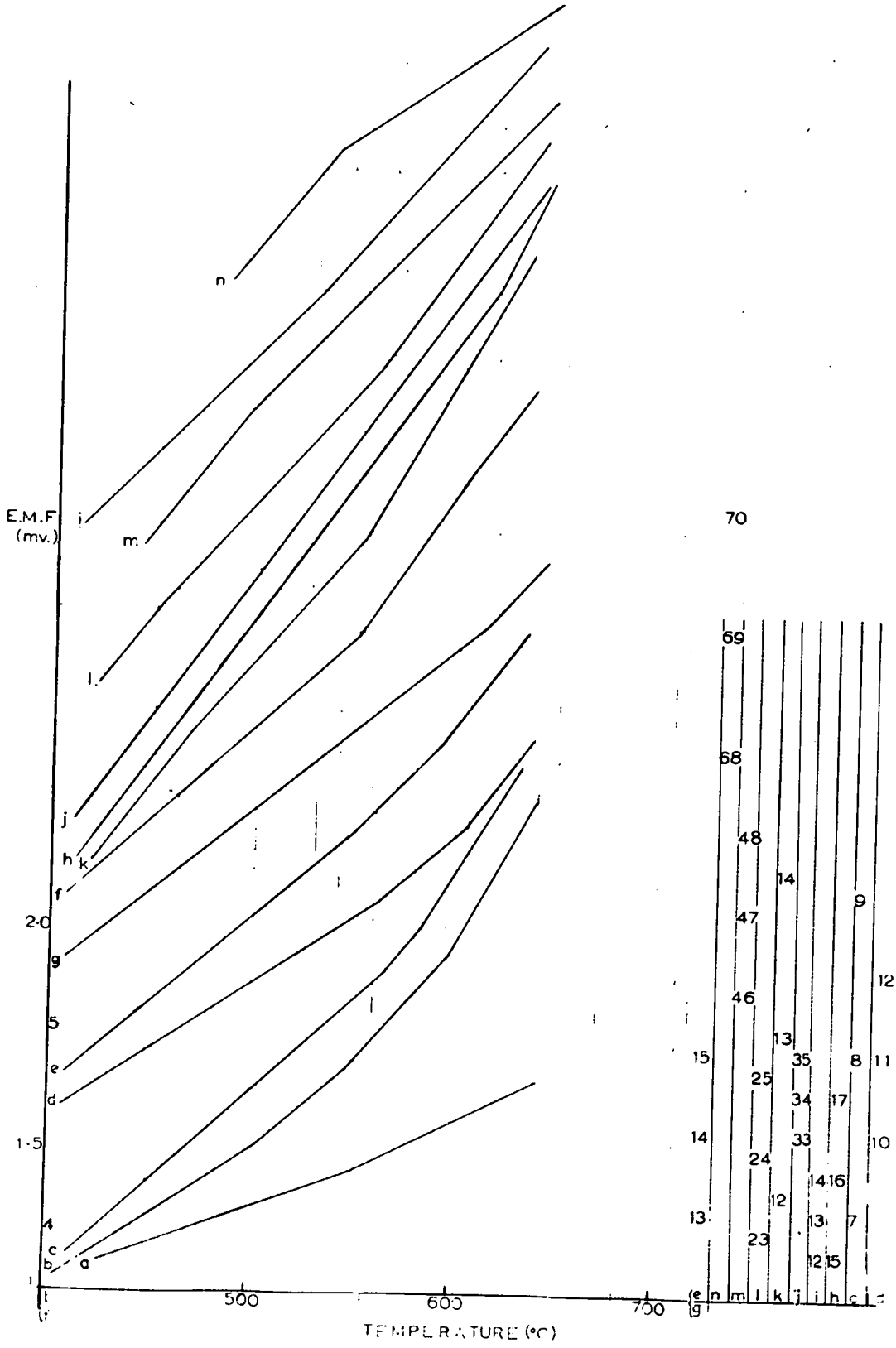
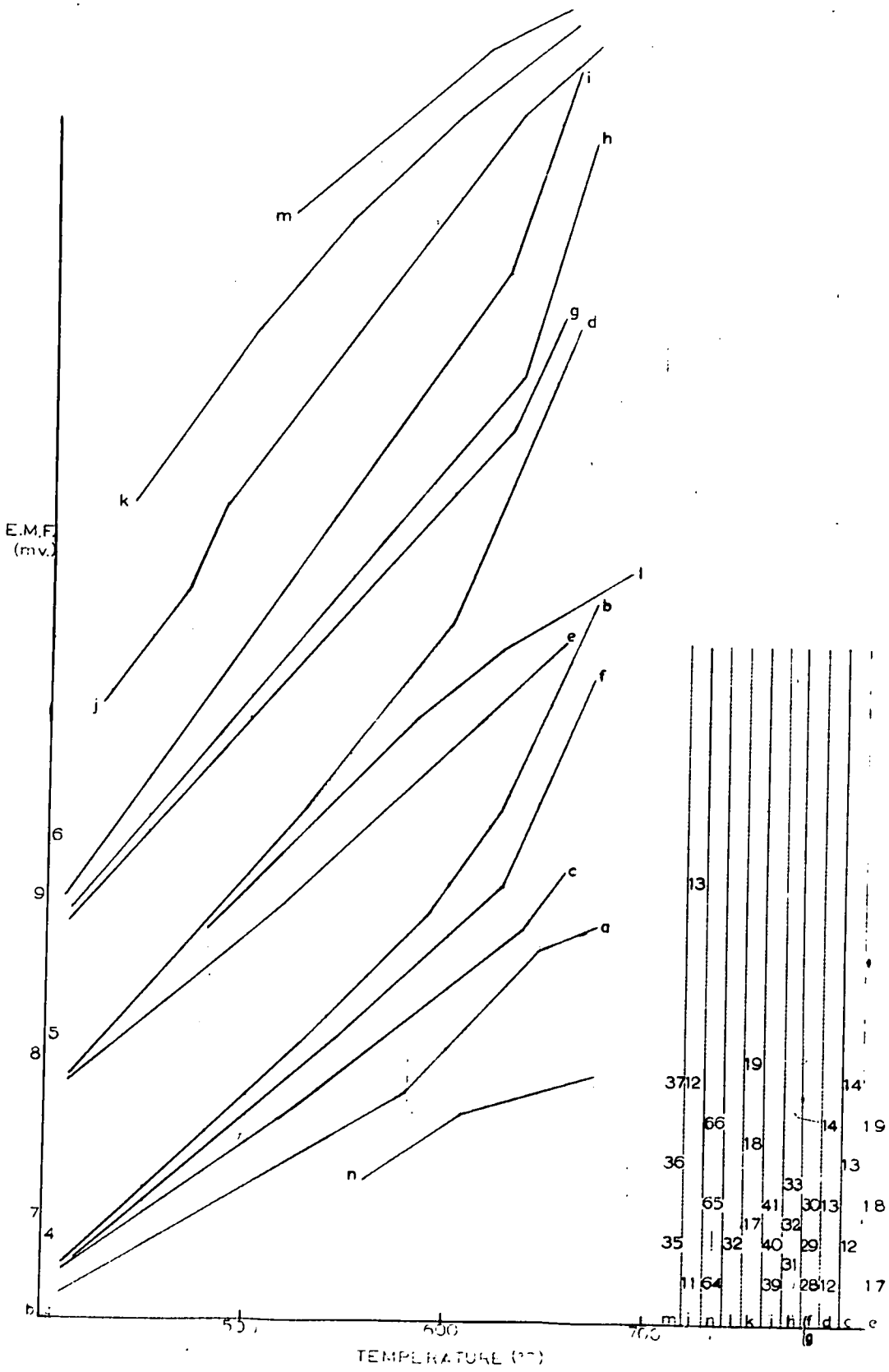

E.M.F (mv.)
2·0
1·5
500
600
700
TEMPERATURE (°C)
70
69
68
48
47
46
14
13
35
25
34
17
33
24
14 16
12
13
23
12 15
9
8
7
12
11
10
15
14
13
a
b
c
d
e
f
g
h
i
j
k
l
m
n

FIGURE 9 (iii)

	x^R	x^B
a	1.00	0.911
b	1.00	0.854
c	1.00	0.786
d	1.00	0.770
e	1.00	0.718
f	1.00	0.655
g	1.00	0.592
h	1.00	0.565
i	1.00	0.532
j	0.532	0.465
k	0.532	0.408
l	0.532	0.363
m	0.532	0.318
n	0.532	0.268

FIGURE 9(iii)


E.M.F.
(m.v.)
TEMPERATURE (°C)
a
b
c
d
e
f
g
h
i
j
k
l
m
n
4
5
6
7
8
9
13
37 12
19
14
66
14
19
18
36
13
33
65
41
30
13
18
17
32
35
32
40
29
12
31
11 64
39
28 12
17
m j n l k i h f d c e
g

FIGURES 9 (iv) and (v)

	x^R	x^B
a	1.00	0.950
b	1.00	0.899
c	1.00	0.863
d	1.00	0.780
e	1.00	0.754
f	1.00	0.705
g	1.00	0.683
h	1.00	0.630
i	1.00	0.617
j	0.617	0.546
k	0.617	0.500
l	0.617	0.465

FIGURE 9(iv)

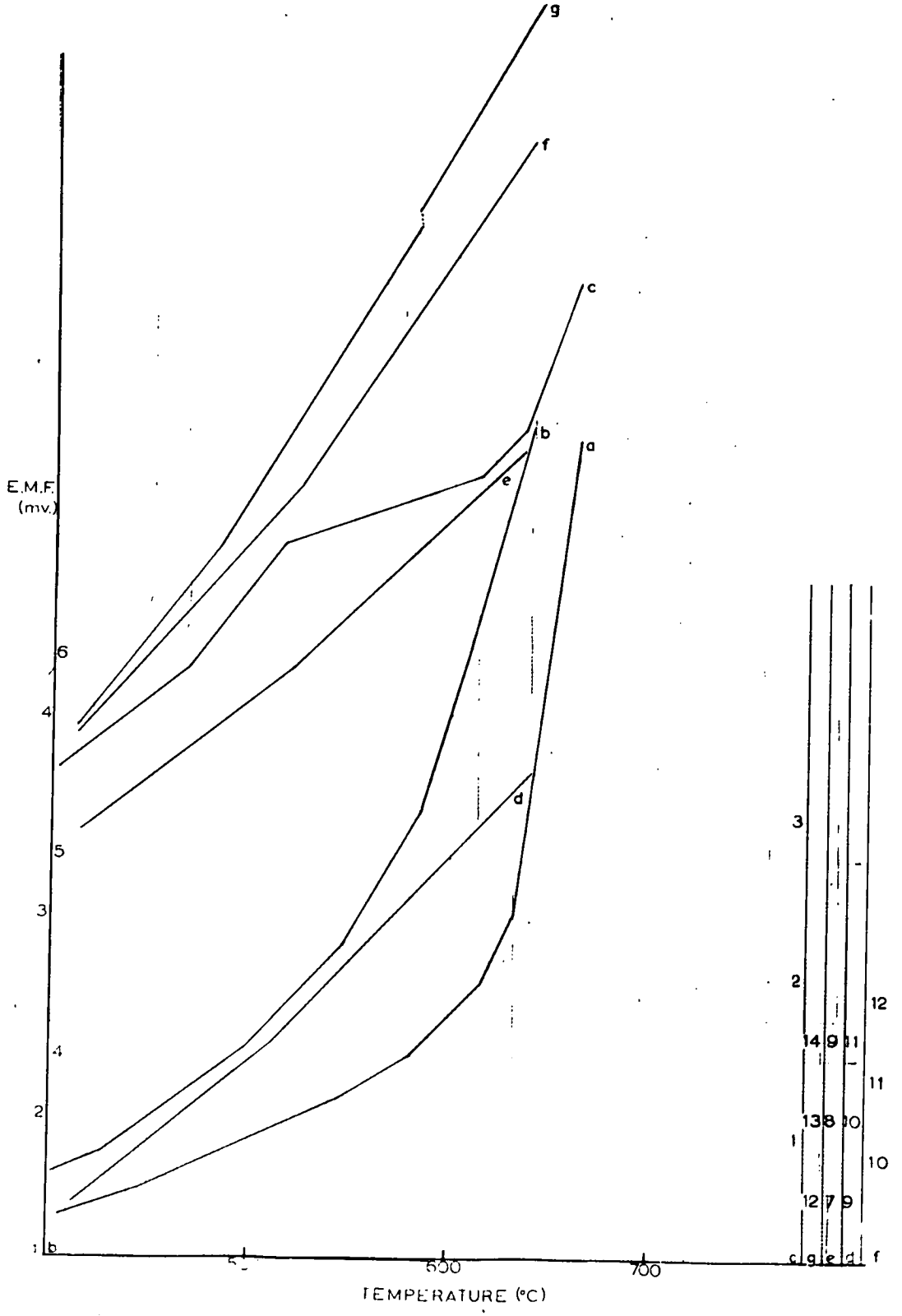

g
f
c
b
a
e
d
E.M.F.
(mv.)
6
4
5
3
4
2
1
b
500
700
TEMPERATURE (°C)
3
2
1
14 9 11
13 8 10
12 7 9
12
11
10
c g e d f

FIGURE 9(v)

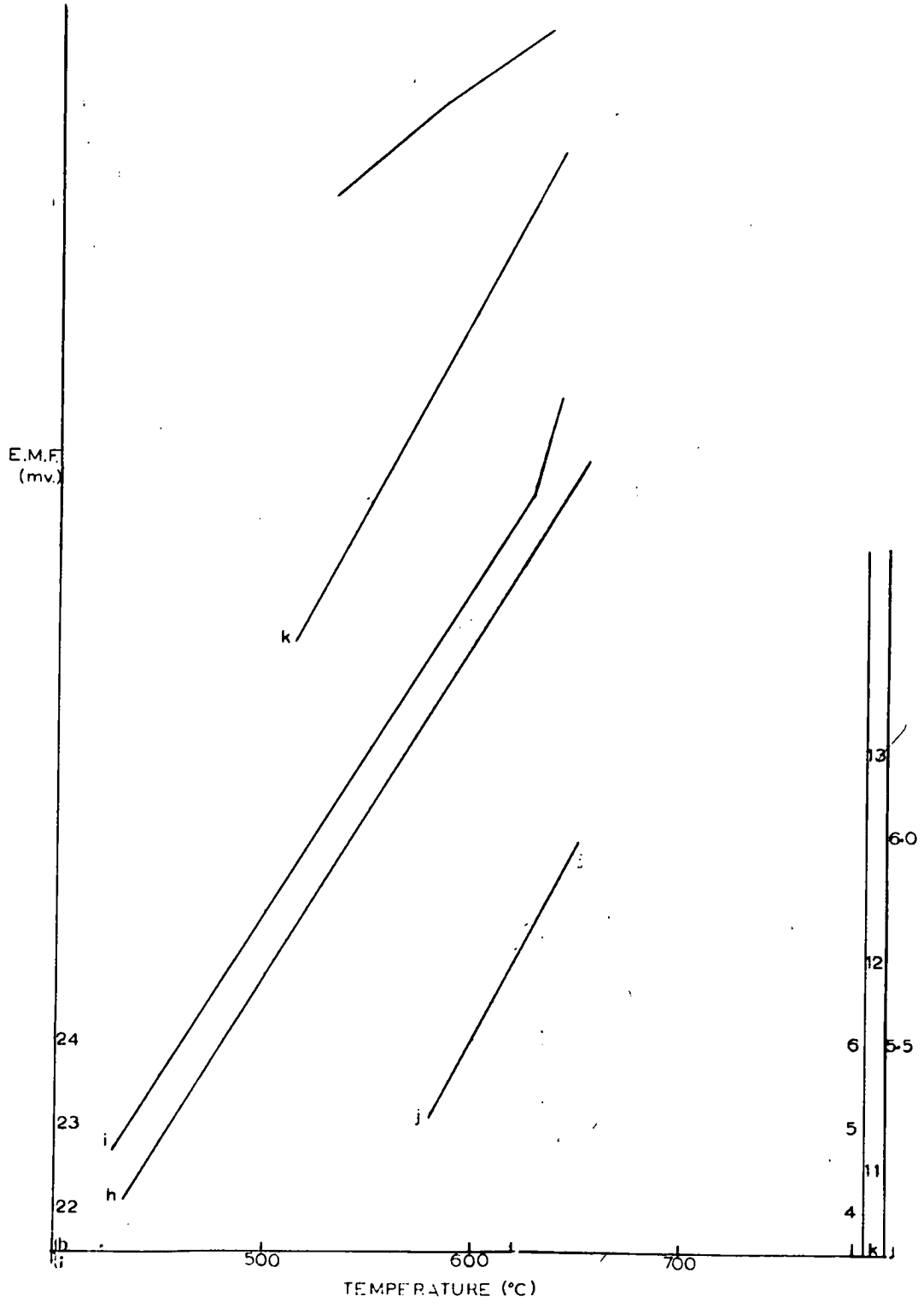


FIGURE 10

Plot of E.M.F. of concentration cells with transference against temperature, for chloride systems.

(i) $PbCl_2$ - CsCl

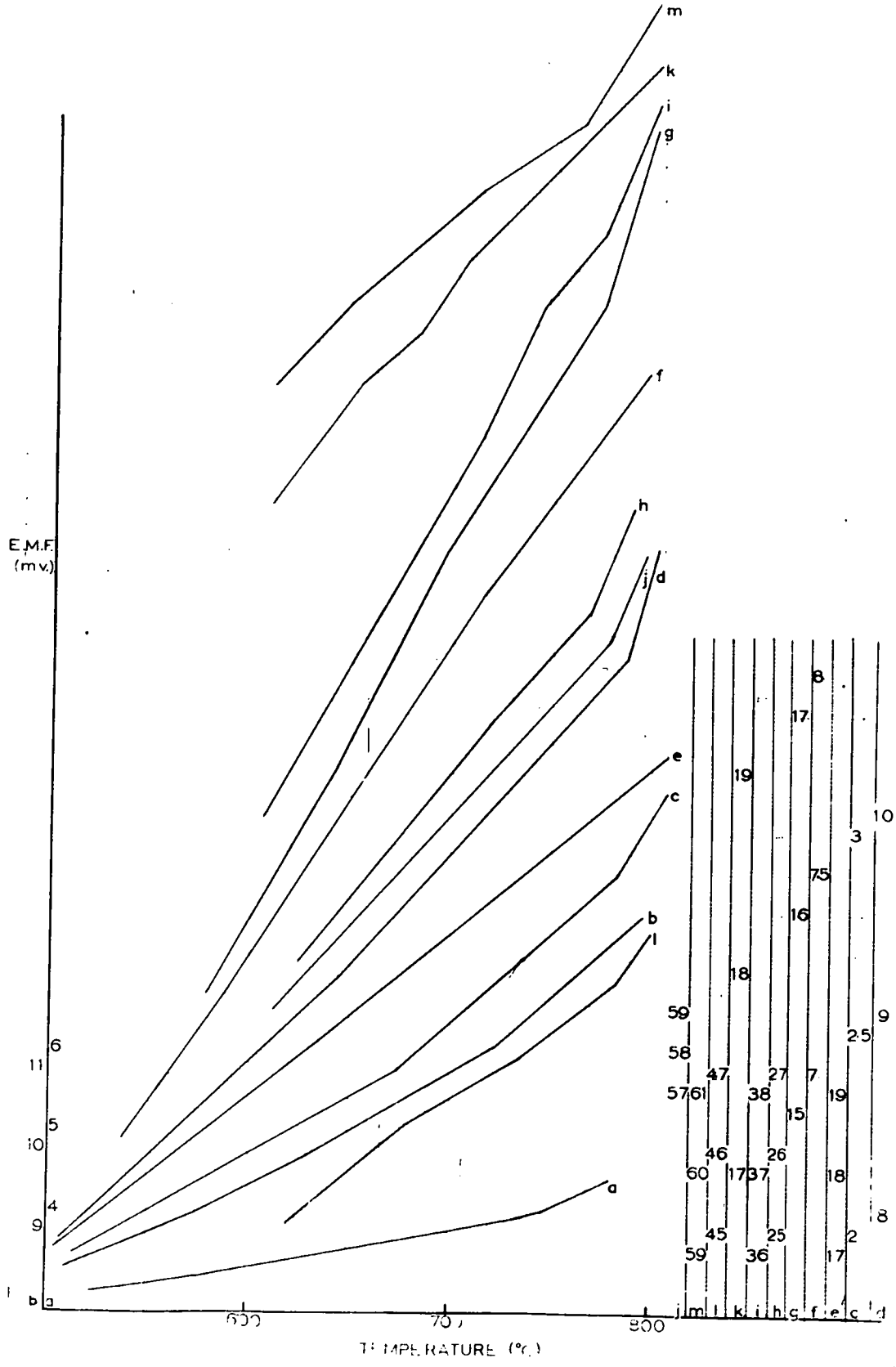
(ii) and (iii) $PbCl_2$ - RbCl.

FIGURE 10 (i)

The letters a, b, etc. specify the mixtures for which the various plots were obtained. The mole-fractions of $PbCl_2$ in the various mixtures are given by x^R, the mole-fraction of $PbCl_2$ in the reference electrolyte and x^B, the mole-fraction of $PbCl_2$ in the bulk electrolyte.

	x^R	x^B
a	1.00	0.908
b	1.00	0.814
c	1.00	0.944
d	1.00	0.843
e	1.00	0.730
f	0.730	0.693
g	0.730	0.644
h	0.730	0.593
i	0.730	0.539
j	0.730	0.493
k	0.493	0.445
l	0.493	0.396
m	0.493	0.347

FIGURE 10(i)



FIGURES 10, (ii) add (iii)

	x^R	x^B
a	1.00	0.955
b	1.00	0.900
c	1.00	0.820
d	1.00	0.759
e	1.00	0.702
f	1.00	0.655
g	1.00	0.569
h	0.569	0.555
i	0.569	0.503
j	0.569	0.455
k	0.569	0.407
l	0.569	0.350
m	0.569	0.314
n	0.569	0.250
o	0.569	0.202

—

FIGURE 10(ii)

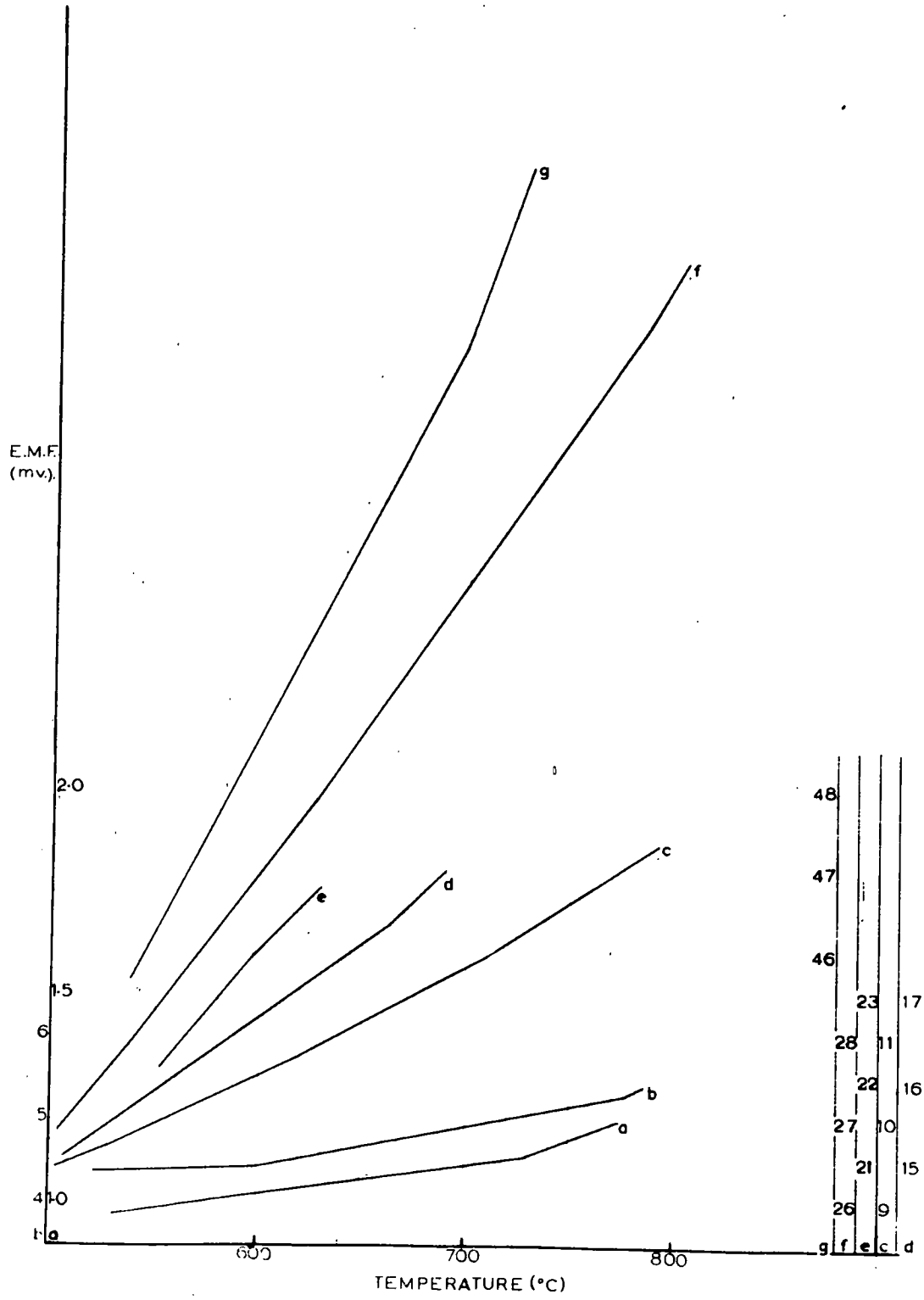

E.M.F.
(mv.).
2·0
1·5
6
5
4·0
h
a
600
700
800
TEMPERATURE (°C)
g
f
e
d
c
b
a
48
47
46
23
17
28
11
22
16
27
10
21
15
26
9
g f e c d

FIGURE 10(iii)

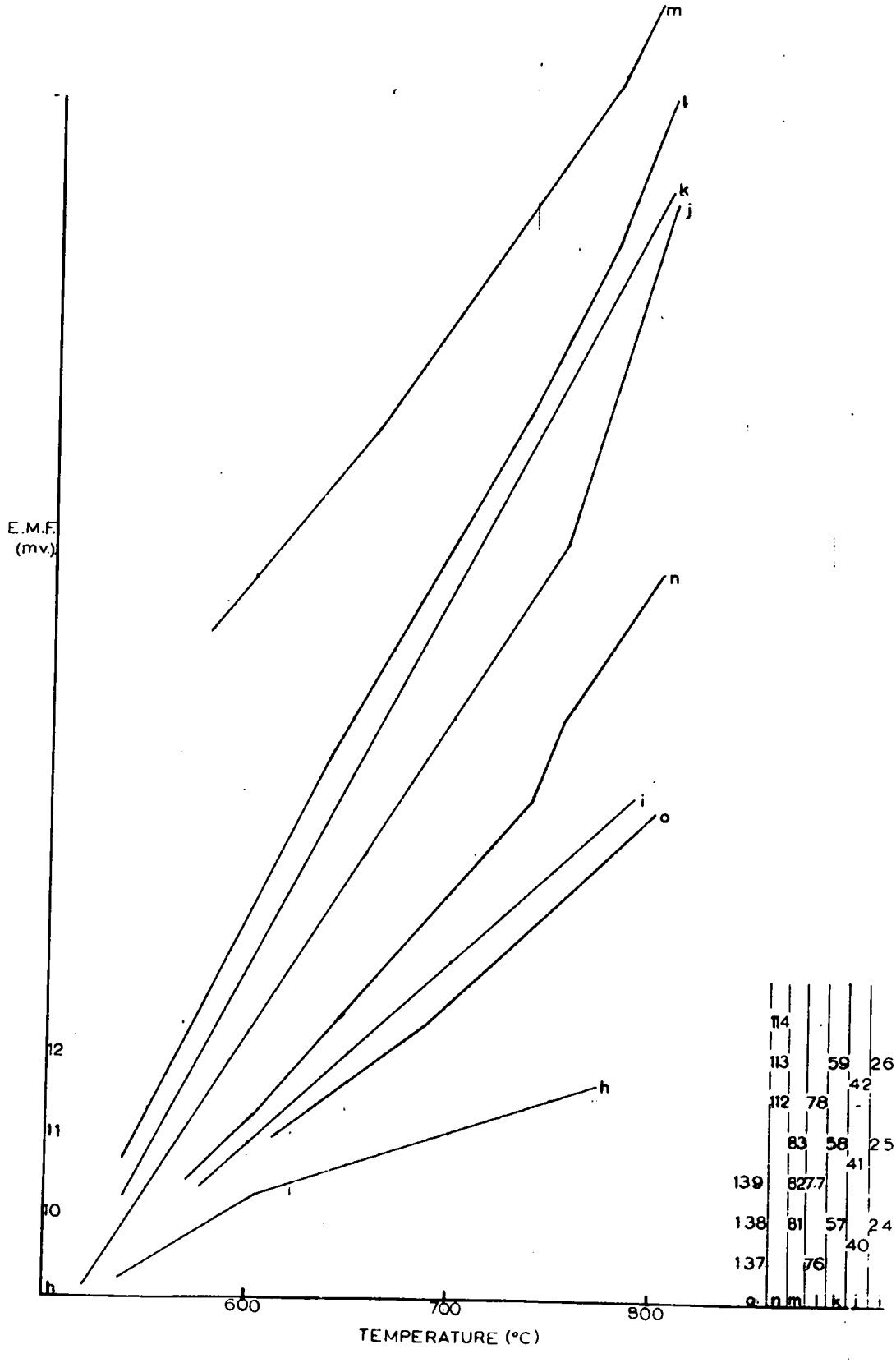


Table 1. (i) : System $PbBr_2$ - Cs Br

x	x'	E.M.F. / Temperature relationships	T_c
0.949	1.000	E_t = -7.629 + 0.0158 T, (640 - 613.8); E_t = -1.061 + 0.0051 T, (613.8-520.7); E_t = -0.280 + 0.0036 T, (520.7 - 408).	613.8, 520.7.
0.888	1.000	E_t = -10.592 + 0.0256T, (638-612.9); E_t = -5.443 + 0.0172T, (612.9-593.7); E_t = -0.693 + 0.0092T, (593.7-495.7); E_t = 0.943 + 0.0059T, (495.7-410).	612.9, 593.7, 495.7.
0.845	1.000	E_t = -11.276 + 0.0320T, (641-619.3); E_t = 0.244 + 0.0134T, (619.3-521.0); E_t = 1.755 + 0.0105T, (521.0-451.4); E_t = 2.387 + 0.0091T, (451.4-418).	619.3, 521.0, 451.4.
0.798	1.000	E_t = -14.328+0.0449T, (643 - 616.2); E_t = 2.681 + 0.0173T, (616.2-470.0); E_t = 4.044 + 0.0144T, (470.0 - 434).	616.2, 470.0.
0.750	1.000	E_t = -9.259 + 0.0449T, (644-626.9); E_t = 4.096 + 0.0236T, (626.9-532.8); E_t = 5.588 + 0.0208T, (532.8 - 434).	626.9, 532.8.
0.700	0.750	E_t = -1.969 + 0.0160T, (648-578.1); E_t = 0.575 + 0.0116T, (578.1-486).	578.1.
0.654	0.750	E_t = 7.507 + 0.0120T, (646-556.2); E_t = 3.113 + 0.0199T, (556.2 - 517).	556.2.
0.603	0.750	E_t = 2.164 + 0.0394T, (652-545).	-
0.550	0.750	E_t = 14.506 + 0.0468T, (651-602.7); E_t = 9.383 + 0.0553T, (602.7-564).	602.7
0.510	0.750	E_t = 40.477 + 0.0371T, (648-616.3); E_t = 23.836 + 0.0641T, (616.3-560).	616.3
0.454	0.510	E_t = 5.771 + 0.0151T, (662 - 564).	-
0.408	0.510	E_t = 23.770 + 0.0220T, (656-616.1); E_t = 25.988 + 0.0184T, (616.1 - 560).	616.1
0.355	0.510	E_t = 50.820 + 0.0166T, (650 - 614.8); E_t = 55.800 + 0.0085T(614.8 - 590.2); E_t = 50.134 + 0.0181T, (590.2 - 564).	614.8, 590.2.

Table 1. (ii) : System $PbBr_2$ - RbBr

x	x'	E.M.F. / temperature relationships	T_c
0.942	1.000	E_t = 0.026 + 0.0025T, (643-548.5); E_t = 0.410 + 0.0018T, (548.5-426)	548.5
0.899	1.000	E_t = -5.541 + 0.0183T, (640-596.8); E_t = -1.423 + 0.0114T, (596.8-547.0); E_t = 0.054 + 0.0087T, (547.0 - 502.8); E_t = 1.110 + 0.0066T, (502.8 - 405)	596.8, 547.0, 502.8
0.842	1.000	E_t = -3.534 + 0.0211T, (632 - 583.7); E_t = -0.148 + 0.0153T, (583.7-563.8); E_t = 2.051 + 0.0114T, (563.8 - 410).	583.7, 563.8
0.800	1.000	E_t = -6.142 + 0.0330T, (638 - 605.3); E_t = 0.395 + 0.0222T, (605.3 - 564.5); E_t = 3.500 + 0.0167T, (564.5 - 406).	605.3, 564.5,
0.744	1.000	E_t = -1.343 + 0.0341T, (634 - 595.0); E_t = 2.763 + 0.0272T, (595.0 - 556.5); E_t = 5.824 + 0.0217T, (556.5 - 408).	595.0, 556.5.
0.694	0.744	E_t = 0.487 + 0.0121T, (635 - 605.5); E_t = -1.269 + 0.0150T, (605.5 - 551.2); E_t = 1.873 + 0.0093T, (551.2 - 406).	605.5, 551.2
0.646	0.744	E_t = -0.720 + 0.0278T, (643 - 614.3); E_t = 3.765 + 0.0205T, (6143 - 407)	614.3
0.597	0.744	E_t = -5.185 + 0.0523T, (642 - 616.5); E_t = 5.296 + 0.0353T, (616.5 - 412)	616.5
0.546	0.744	E_t = 5.762 + 0.0572T, (636 - 528.7); E_t = 8.829 + 0.0514T, (528.7 - 412)	528.7
0.500	0.744	E_t = 11.972 + 0.0700T, (638 - 410)	-
0.444	0.500	E_t = 3.829 + 0.0222T, (632 - 552.6); E_t = 8.029 + 0.0146T, (552.6 - 467.7); E_t = 7.000 + 0.0168T, (467.7 - 420).	552.6, 467.7
0.398	0.500	E_t = 13.683 + 0.0360T, (638 - 558.7); E_t = 18.041 + 0.0282T, (558.7 - 452.1); E_t = 16.368 + 0.0319T, (452.1 - 422).	558.7, 452.1
0.348	0.500	E_t = 40.199 + 0.0264T, (642 - 494.7); E_t = 37.082 + 0.0327T, (494.7 - 422)	494.7
0.300	0.500	E_t = 66.287 + 0.0172T, (644 - 534.6); E_t = 58.851 + 0.0311T, (534.6 - 482)	534.6

Table 1. (iii) : System $PbBr_2$ - KBr.

x	x^1	E.M.F. / temperature relationships	T_c
0.911	1.000	$E_t = 2.553 + 0.0045\,T$, (676 - 643.9); $E_t = -1.697 + 0.0111T$, (643.9-579.0); $E_t = 1.314 + 0.0059\,T$, (579.0-408);	643.9, 579.0
0.854	1.000	$E_t = -8.215 + 0.0284T$, (675 - 628.0); $E_t = -1.809 + 0.0182T$, (628 .0-590.4); $E_t = 1.085 + 0.0133T$, (590.4-530.6); $E_t = 1.934 + 0.0117T$, (530.6-410)	628.0, 590.4, 530.6.
0.786	1.000	$E_t = -5.626 + 0.0338T$, (658 - 636.2); $E_t = 3.153 + 0.0200T$, (636.2 - 526.6) $E_t = 4.417 + 0.0176T$, (526.6 - 408)	636.2, 526.6
0.770	1.000	$E_t = 4.384 + 0.0238T$, (658 - 517.4); $E_t = 5.781 + 0.0211T$, (517.4 - 411)	517.4
0.718	1.000	$E_t = -15.276 + 0.0674T$, (662 - 601.6); $E_t = 5.782 + 0.0324T$, (601.6 - 528.2) $E_t = 7.578 + 0.0290T$, (528.2 - 412)	601.6, 528.2.
0.655	1.000	$E_t = -35.456 + 0.1170T$, (672 - 627.0); $E_t = 8.503 + 0.0469T$, (627.0 - 545.4) $E_t = 10.521 + 0.0432T$, (545.4 - 410)	627.0, 545.4
0.592	1.000	$E_t = -22.299 + 0.1140T$, (654 - 629.1); $E_t = 13.438 + 0.0572\,T$, (629.1 - 410)	629.1
0.565	1.000	$E_t = -45.034 + 0.1554T$, (668 - 631.5); $E_t = 14.838 + 0.0606T$, (631.5 - 412)	631.5
0.532	1.000	$E_t = -31.097 + 0.1525T$, (660 - 625.2); $E_t = 18.985 + 0.0724T$, (625.2 - 408)	625.2
0.465	0.532	$E_t = 11.426 + 0.0086T$, (670 - 631.2); $E_t = 8.270 + 0.0136T$, (631.2 - 486.2) $E_t = 3.894 + 0.0226T$, (486 .2 - 466.9); $E_t = 8.050 + 0.0137T$, (466.9 - 426)	631.2, 486.2, 466.9.
0.403	0.532	$E_t = 20.278 + 0.0160T$, (658 - 599.7); $E_t = 18.059 + 0.0197T$, (599.7-546.0) $E_t = 15.711 + 0.0240T$, (546.0 - 499.2); $E_t = 13.165 + 0.0291T$, (499.2 - 440)	599.7, 546.0, 499.2.
0.363	0.532	$E_t = 29.918 + 0.0152T$, (690 - 624.1); $E_t = 26.298 + 0.0210T$, (624.1 - 583.8), $E_t = 23.554 + 0.0257T$, (583.8 - 498.2); $E_t = 19.518 + 0.0338T$, (498.2 - 480).	624.1, 583.8, 498.2.
0.318	0.532	$E_t = 41.572 + 0.0136T$, (654 - 614.4); $E_t = 36.718 + 0.0215T$, (614.4 - 518)	614.4
0.268	0.532	$E_t = 61.470 + 0.0076T$, (675 - 607.5); $E_t = 55.516 + 0.0174T$, (607.5 - 560)	607.5.

Table 1. (iv) : System $PbBr_2$ - NaBr

x	x'	E.M.F. / temperature relationships	T_c
0.950	1.000	E_t = -45.466 + 0.767T, (663 - 632.1); E_t = -10.507 + 0.0214T, (632.1-615.7)	632.1, 615.7,
		E_t = -3.673 + 0.0103T, (615.7 - 580.4); E_t = -1.235 + 0.0061T, (580.4 - 544.7)	580.4, 544.7
		E_t = -0.309 + 0.0044Tk (544.7 - 444.4); E_t = 0.091 + 0.0046T, (444.4 - 405)	444.4.
0.899	1.000	E_t = -31.609 + 0.0618T, (640 - 608.5); E_t = -13.597 + 0.0322T, (608.5 - 584.8)	608.5, 584.8,
		E_t = -5.001 + 0.0175T, (584.8 - 545.5); E_t = -1.182 + 0.0105T, (545.5 - 496.3)	545.5, 496.3,
		E_t = 0.456 + 0.0072T, (496.3 - 428.4); E_t = 1.570 + 0.0046T, (428.4 - 402)	428.4.
0.863	1.000	E_t = -36.654 + 0.0701T, (662 - 635.3); E_t = -8.761 + 0.0262T, (635.3 - 612..6)	635.3, 612.6,
		E_t = 1.838 + 0.0089T, (612.6 - 515.5); E_t = -10.330 + 0.0325T, (515.5 - 467.3)	515.5, 467.3.
		E_t = -4.208 + 0.0194T, (467.3 - 403).	
0.780	1.000	E_t = -2.354 + 0.0260T, (642 - 509.5); E_t = 0.754 + 0.0199T, (509.5 - 412)	509.5
0.754	1.000	E_t = 1.193 + 0.0239T, (635 - 518.0); E_t = 3.628 + 0.0192T, (518.0 - 414)	518.0
0.705	1.000	E_t = -1.437 + 0.0379T, (638 - 523.8); E_t = 3.697 + 0.0281T, (523.8 - 412)	523.8
0.683	1.000	E_t = -0.311 + 0.0425T, (642 ~ 580)*; E_t = 0.335 + 0.0410T, (~ 580-482.9)*;	482.9
		E_t = 4.730 + 0.0319T, (482.9 - 412).	
0.630	1.000	E_t = 4.680 + 0.0403T, (654 - 433).	-
0.617	1.000	E_t = -25.405 + 0.0893T, (641 - 627.7); E_t = 5.795 + 0.0396T, (627.7 - 448).	627.7
0.546	0.617	E_t = -0.187 + 0.0095T, (650 - 580).	-
0.500	0.617	E_t = 3.985 + 0.0186T, (642 - 514).	-
0.465	0.617	E_t = 7.141 + 0.0175T, (636 - 583.2); E_t = 4.983 + 0.0212T, (583.2 - 531).	583.2

* This pair of lines was observed not to intersect - a discontinuity in E.M.F. was in fact observed, at approximately 580° C.

Table 2. (i) : System $PbCl_2$ - CsCl

x	x'	E.M.F. / temperature relationships	T_c
0.908	1.000	$E_t = -4.484 + 0.0114T$, (780 - 745.2); $E_t = -0.907 + 0.0066T$, (745.2-726.5) $E_t = 0.546 + 0.0046T$, (726.5 - 574.3); $E_t = 1.350 + 0.0032T$, (574.3 - 522).	745.2, 726.5, 574.3.
0.814	1.000	$E_t = -4.727 + 0.0222T$, (797 - 721.6); $E_t = 0.613 + 0.0148T$, (721.6 - 628.1) $E_t = 1.995 + 0.0126T$, (628.1 - 573.5); $E_t = 3.142 + 0.0106T$, (573.5 - 508).	721.6, 628.1, 573.5
0.944	1.000	$E_t = -3.446 + 0.0081T$, (808 - 782.2); $E_t = -0.630 + 0.0045T$, (782.2 - 672.3); $E_t = 0.513 + 0.0028T$, (672.3 - 512).	782.2, 672.3,
0.843	1.000	$E_t = -16.850 + 0.0351T$, (803 - 787.1); $E_t = 1.885 + 0.0133T$, (787.1 - 643.8); $E_t = 3.044 + 0.0095T$, (643.8 - 507).	787.1, 643.8
0.730	1.000	$E_t = 6.344 + 0.0209T$, (808 - 634.6); $E_t = 7.169 + 0.0196T$, (634.6 - 504).	634.6.
0.693	0.730	$E_t = 3.341 + 0.0068T$, (798 - 716.4); $E_t = 2.553 + 0.0079T$, (716.4 - 586.6), $E_t = 2.905 + 0.0073T$, (586.6 - 537).	716.4, 586.6
0.644	0.730	$E_t = -9.086 + 0.0363T$, (800 - 776.7); $E_t = 6.604 + 0.0161T$, (776.7 - 697.0), $E_t = 3.746 + 0.0202T$, (697.0 - 642.5); $E_t = 5.352 + 0.0177T$, (642.5 - 578).	776.7, 697.0, 642.5
0.593	0.730	$E_t = 1.684 + 0.0405T$, (800 - 768.5); $E_t = 10.368 + 0.0292T$, (768.5 - 716.9), $E_t = 8.504 + 0.0318T$, (716.9 - 624).	768.5, 716.9
0.539	0.730	$E_t = 1.685 + 0.0609T$, (801 - 773.1); $E_t = 25.499 + 0.0301T$, (773.1 - 743.5), $E_t = 7.356 + 0.0545T$, (743.5 - 713.2); $E_t = 14.488 + 0.0445T$, (713.2- 605)	773.1, 743.5, 713.2
0.493	0.730	$E_t = -25.009 + 0.1199T$, (797 - 778.8); $E_t = 24.759 + 0.0560T$, (778.8 - 612).	778.8
0.445	0.493	$E_t = 14.631 + 0.0099T$, (801 - 708.0); $E_t = 10.666 + 0.0155T$, (708.0 - 681.2) $E_t = 14.890 + 0.0093T$, (681.2 - 650.2); $E_t = 11.899 + 0.0139T$, (650.2-608).	708.0, 681.2, 650.2,
0.396	0.493	$E_t = 20.258 + 0.0356T$, (800 - 782.4); $E_t = 32.621 + 0.0198T$, (782.4 - 736.0) $E_t = 36.154 + 0.0150T$, (736.0 - 677.6); $E_t = 31.817 + 0.0214T$, (677.6 - 619).	782.4, 736.0, 677.6.
0.347	0.493	$E_t = 42.245 + 0.0406T$, (800 - 763.1); $E_t = 60.407 + 0.0168T$, (763.1 - 711.6) $E_t = 56.635 + 0.0221T$, (711.6 - 646.1); $E_t = 53.081 + 0.0276T$, (646.1 - 609)	763.1, 711.6, 646.1.

Table 2. (ii) : System $PbCl_2$ - RbCl

x	x'	E.M.F. / temperature relationships	Tc
0.955	1.000	$E_t = -0.271 + 0.0019T$, (774 - 728.3), $E_t = 0.603 + 0.0007T$, (728.3 - 531).	728.3
0.900	1.000	$E_t = -4.329 + 0.0124T$, (786 - 776.8), $E_t = 1.497 + 0.0049T$, (776.8 - 597.8) $E_t = 4.008 + 0.0007T$, (597.8 - 522).	776.8, 597.8
0.820	1.000	$E_t = 0.432 + 0.0163T$, (793 - 709.1); $E_t = 2.134 + 0.0139T$, (709.1 - 619.1), $E_t = 3.558 + 0.0116T$, (619.1 - 527.3); $E_t = 4.138 + 0.0105T$, (527.3 - 503).	709.1, 619.1, 527.3
0.759	1.000	$E_t = 1.345 + 0.0249T$, (690 - 663.3); $E_t = 5.922 + 0.0180T$, (663.3 - 506).	663.3
0.702	1.000	$E_t = 8.256 + 0.0255T$, (630 - 597.0); $E_t = 5.271 + 0.0305T$, (597.0 - 552).	597.0
0.655	1.000	$E_t = 3.829 + 0.0418T$, (804 - 785.0); $E_t = 7.990 + 0.0365T$, (785.0 - 626.6) $E_t = 10.058 + 0.0332T$, (626.6 - 537.8), $E_t = 11.080 + 0.0313T$, (537.8 - 504).	785.0, 626.6, 537.8
0.569	1.000	$E_t = 3.184 + 0.0720T$, (728 - 696.3); $E_t = 19.758 + 0.0482T$, (696.3-538).	696.3
0.555	o.569	$E_t = 5.181 + 0.0084T$, (794 - 604.0); $E_t = 1.013 + 0.0153T$, (604.0 - 537).	604.0
0.503	0.569	$E_t = 11.178 + 0.0229T$, (790 - 576).	-
0.455	0.569	$E_t = -13.170 + 0.0819T$, (808 - 755.2); $E_t = 18.928 + 0.0394T$, (755.2-520).	755.2
0.407	0.569	$E_t = 31.657 + 0.0475T$, (805 - 538).	-
0.350	0.569	$E_t = 32.270 + 0.0661T$, (807 - 778.2); $E_t = 49.487 + 0.0504T$, (778.2 - 735.2), $E_t = 53.972 + 0.0443T$, (735.2 - 638.2); $E_t = 50.334 + 0.0500T$, (638.2- 538).	778.2, 735.2, 638.2
0.314	0.569	$E_t = 29.672 + 0.1025T$, (799 - 778.8); $E_t = 52.260 + 0.0735T$, (778.8 - 659.9), $E_t = 59.849 + 0.0620T$, (659.9 - 578).	778.8, 659.9,
0.250	0.569	$E_t = 64.093 + 0.0760T$, (804 - 754.0); $E_t = 22.924 + 0.1306T$, (754.0-739.1), $E_t = 76.437 + 0.0582T$, (739.1 - 602.0); $E_t = 81.855 + 0.0492T$, (602.0-570).	754.0, 739.1, 602.0
0.202	0.569	$E_t = 110.048 + 0.0476T$, (801 - 685.8); $E_t = 117.317 + 0.0370T$, (685.8 - 615).	685.8

(ii) Composition Dependence of E.M.F.

The dependence of cell E.M.F. on composition of the bulk electrolyte is shown in Figures 11, (i) to (iv), where E.M.F. (mv.) is plotted against mole fraction of alkali bromide. Figure 11 (v) shows a comparison of the 550° C, isotherms for the four bromide systems investigated, while the isotherms for the two chloride systems are shown in Figures 12 (i) and (ii).

The values of E.M.F. were obtained, in all cases, by interpolation of the computed E.M.F. / temperature relationships. In every case, the curves were drawn, as nearly as possible, through all the points.

A more sensitive test of E.M.F. dependence on composition is provided by plots of cell E.M.F. against -log (mole fraction PbX_2) . These plots are shown in Figures 13, (i) to (iv) for the bromide systems and Figures 14 (i) and (ii), for the chlorides. They were obtained as follows : For a given system (and mixture) the values of E.M.F. at various temperatures (at intervals of 50°C) were deduced by interpolation of the computed E.M.F. / temperature relationships. The E.M.F. versus -log x_{PbX_2} isotherms were then plotted at the various temperatures, and by inspection the lines of best fit drawn. For each collinear series of points $\left[E,\ -\log x_{PbX_2}\right]$, the line of best fit was calculated, using an Elliott 503 computer and a slightly modified version of the programme given in Appendix 1.

The equations to the lines corresponding to values of $-\log x_{PbX_2}$ close to zero were not obtained in this way, because of the condition that E must be zero at $-\log x_{PbX_2} = 0$ (i.e. pure PbX_2). In this region the line of best fit was drawn as accurately as possible by inspection, and its gradient measured.

The compositions at which changes of slope occurred were calculated from the computed and estimated equations to the lines.

In Figures 13 and 14 the experimental points are not plotted because the deviations from the straight lines were in general very small. For the 650°C E.M.F. / $-\log x_{PbBr_2}$ isotherm, for the system $PbBr_2$ - NaBr (Figure 13 (iv)) the spread of the experimental points was greater and it was felt that a single straight line gave a better representation of the relationship between the points than did a series of intersecting lines. In this case, therefore, the line of best fit for all the points was computed. The "computed line" is slightly in error - the intercept on the E.M.F. axis is -0.253 mv. instead of the true value 0.0 mv. In all other cases, representation of the data as a series of straight lines was fully justified, because the mean deviation of the points from linearity, in any linear region, was much less than the relative changes in slope.

In Tables 3, (i) to (iv) and 4, (i) and (ii) the equations to the linear regions are presented, together with the compositions (mole fraction of PbX_2), denoted by x_c, at which changes of slope occur. In Tables 3 and 4 the variable $-\log x_{PbX_2}$ is denoted by P, and T is the temperature (in degrees Centigrade) appropriate to each isotherm.

The figures in parentheses indicate the region of applicability (i.e. the range of $- \log x_{PbX_2}$) of each linear equation.

FIGURE 11.

Plot of E.M.F. of concentration cells with transference against mole fraction of alkali halide, for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr

(iv) $PbBr_2$ - NaBr

(v) Comparison of the 550°C isotherms for the four bromide systems.

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 11(i)

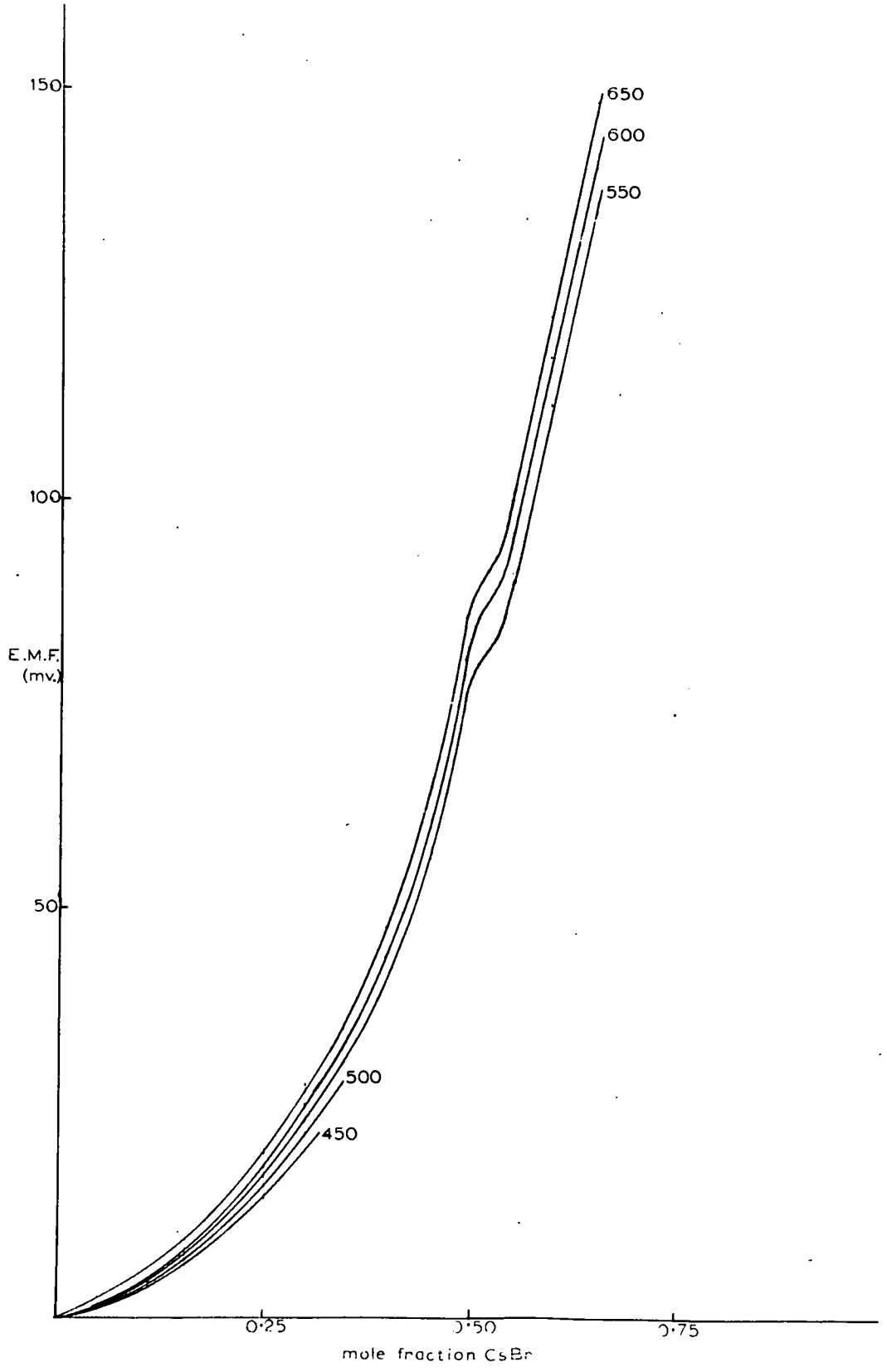

150
100
50
E.M.F.
(mv.)
650
600
550
500
450
0·25
0·50
0·75
mole fraction CsBr

FIGURE 11(ii)

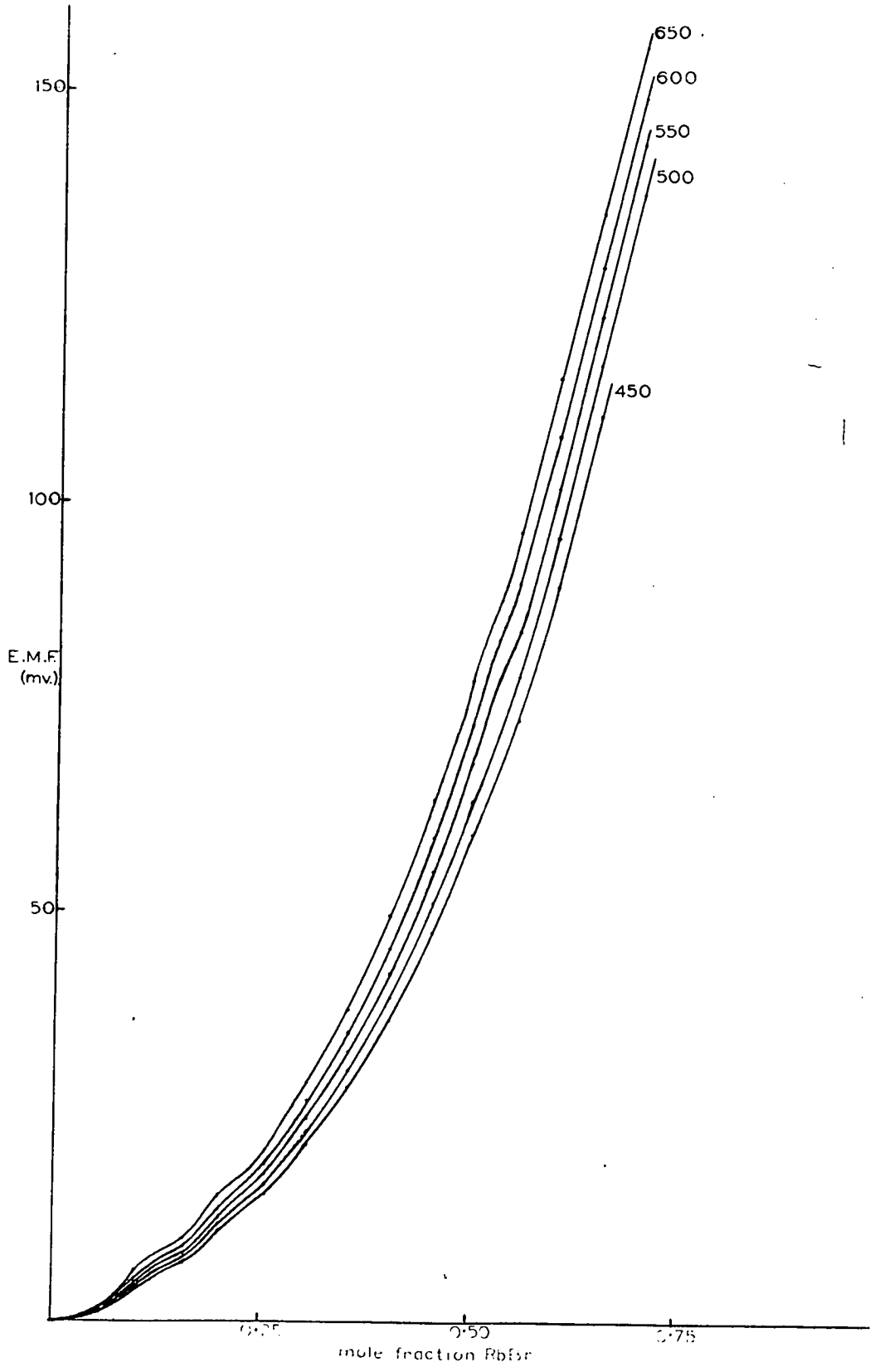

650
600
550
500
450
150
100
50
E.M.F
(mv.)
0·50
0·75
mole fraction RbBr

FIGURE 11(iii)

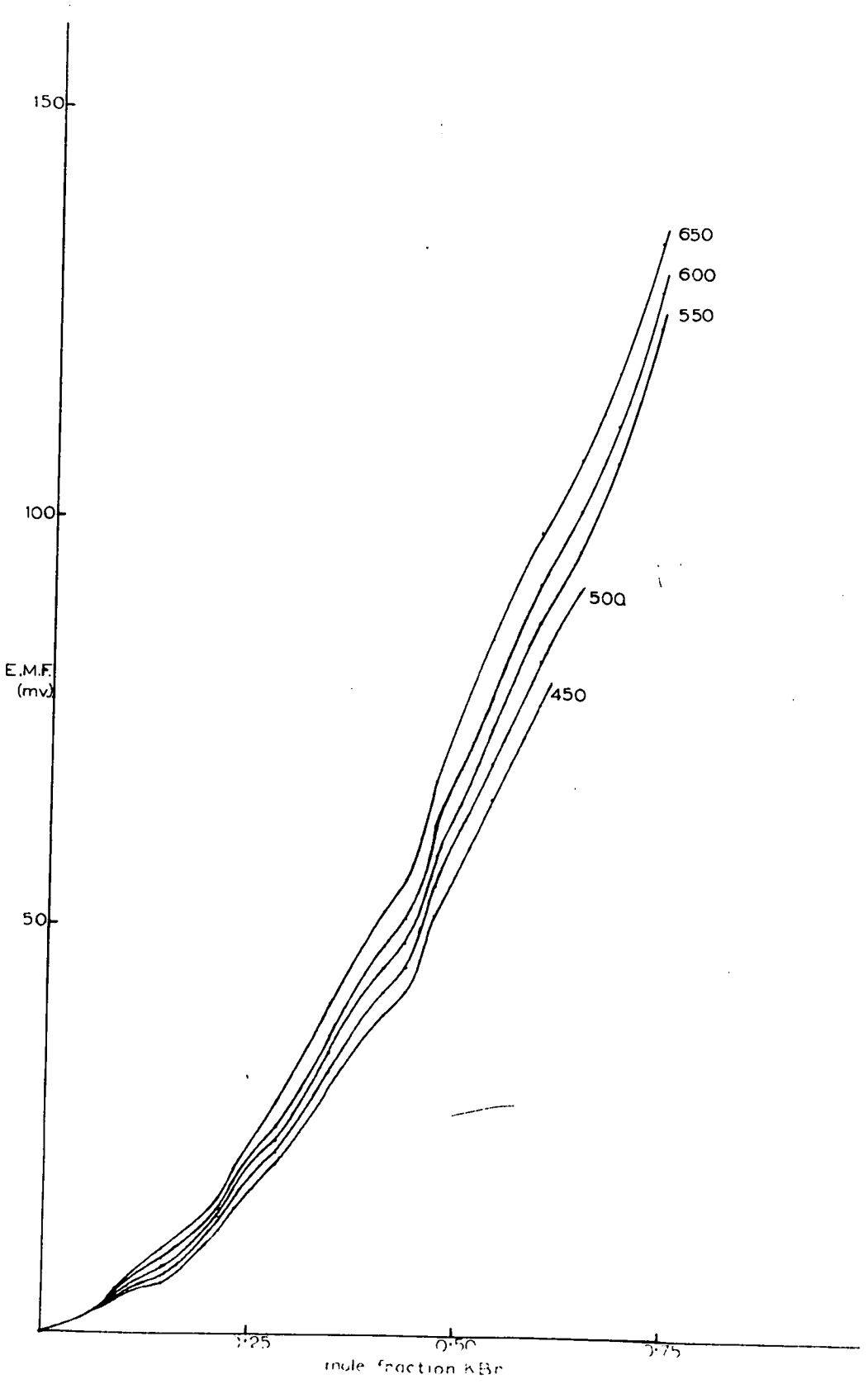


FIGURE II(a)

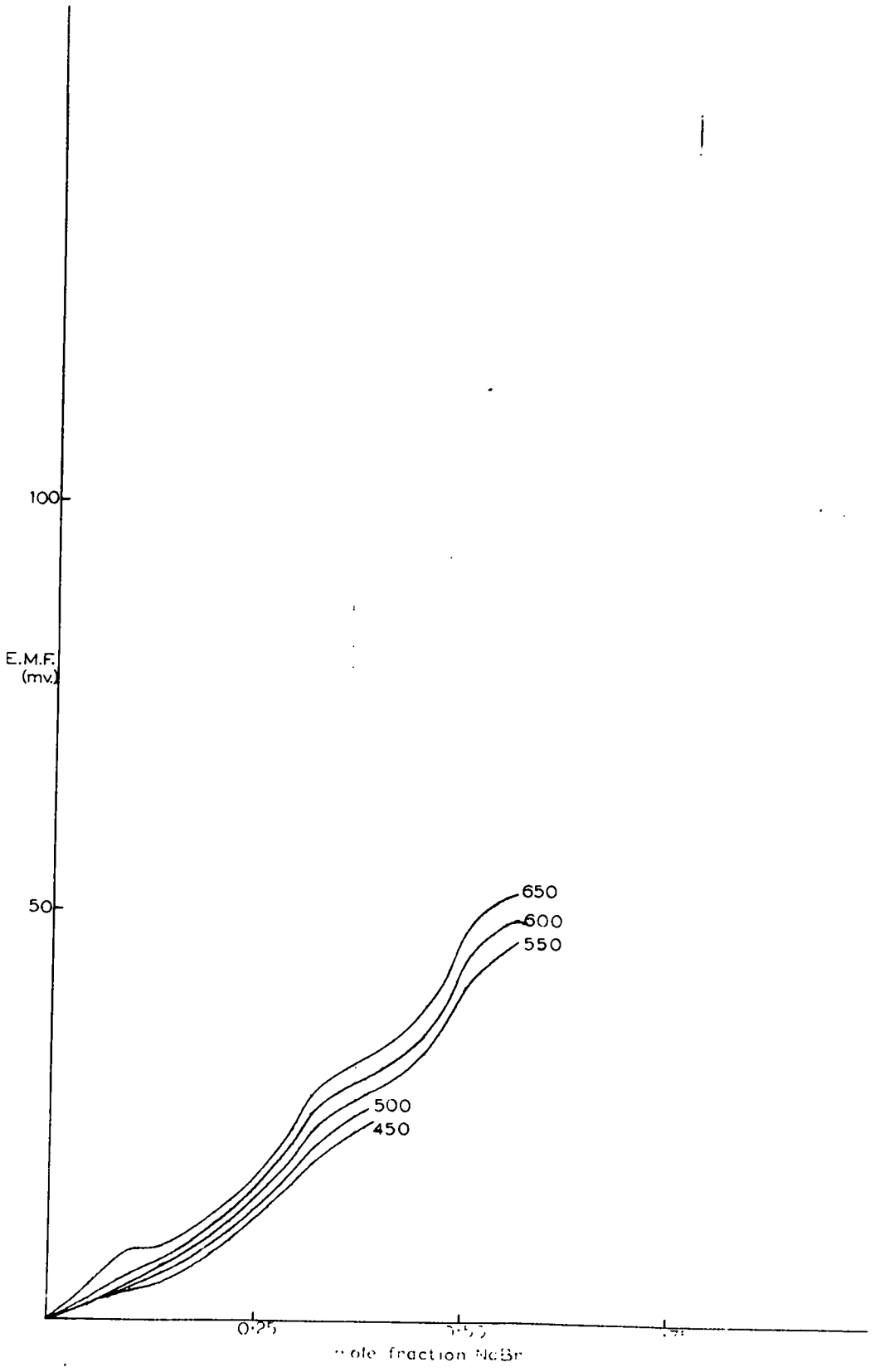


FIGURE 11(v)

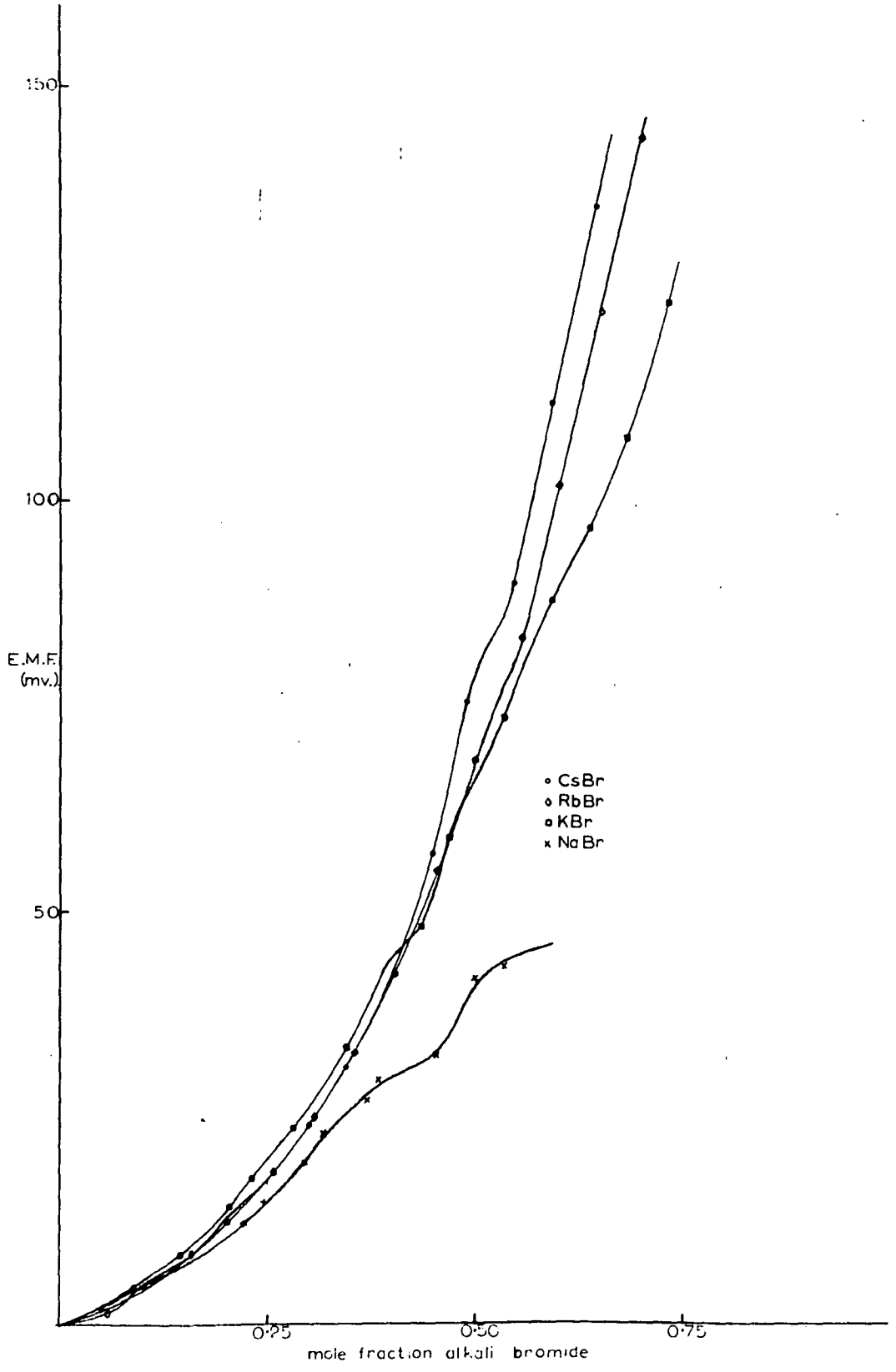

150
100
50
E.M.F.
(mv.)
CsBr
RbBr
KBr
NaBr
0·25
0·50
0·75
mole fraction alkali bromide

FIGURE 12.

Plot of E.M.F. of concentration cells with transference against mole fraction of alkali halide, for chloride systems.

(i) $PbCl_2$ - CsCl

(ii) $PbCl_2$ - RbCl.

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 12 (i)

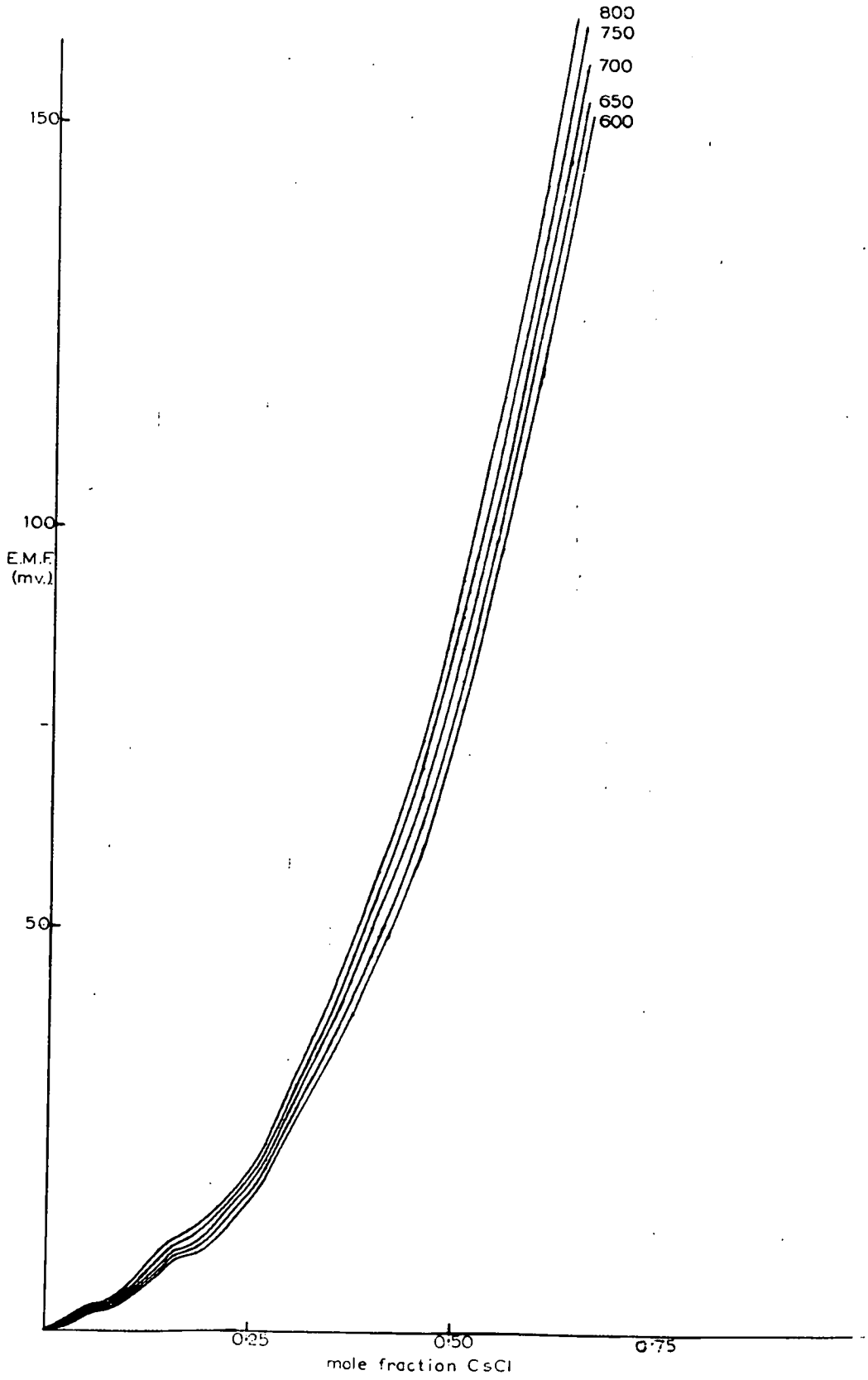

800
750
700
650
600
150
100
E.M.F.
(mv.)
50
0·25
0·50
0·75
mole fraction CsCl

FIGURE 12(ii)

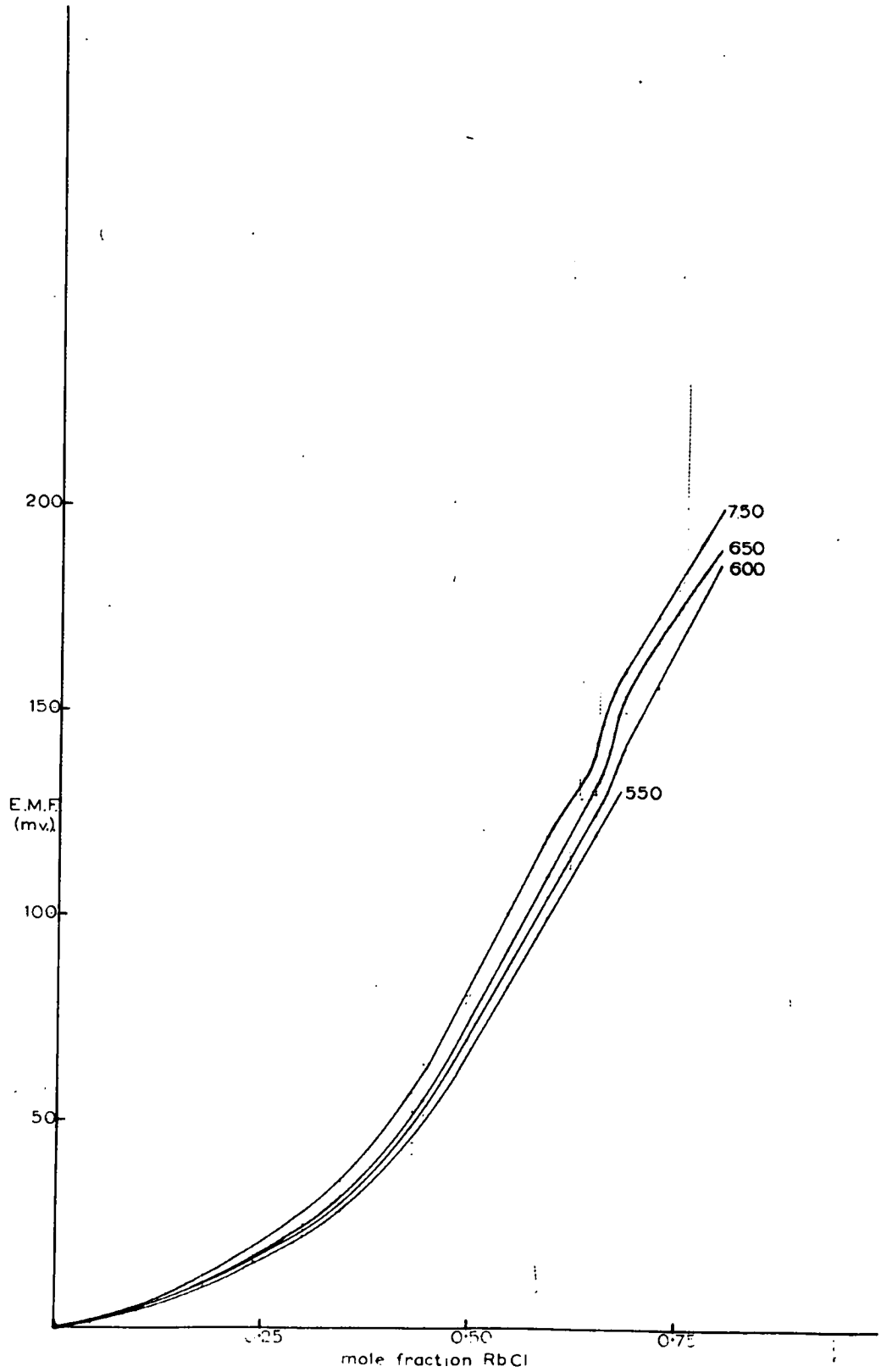

200
150
100
50
E.M.F.
(mv.)
750
650
600
550
0·25
0·50
0·75
mole fraction RbCl

FIGURE 13.

Plot of E.M.F. of concentration cells with transference against the negative logarithm of the mole fraction of lead halide for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr

(iv) $PbBr_2$ - NaBr

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 13(i)

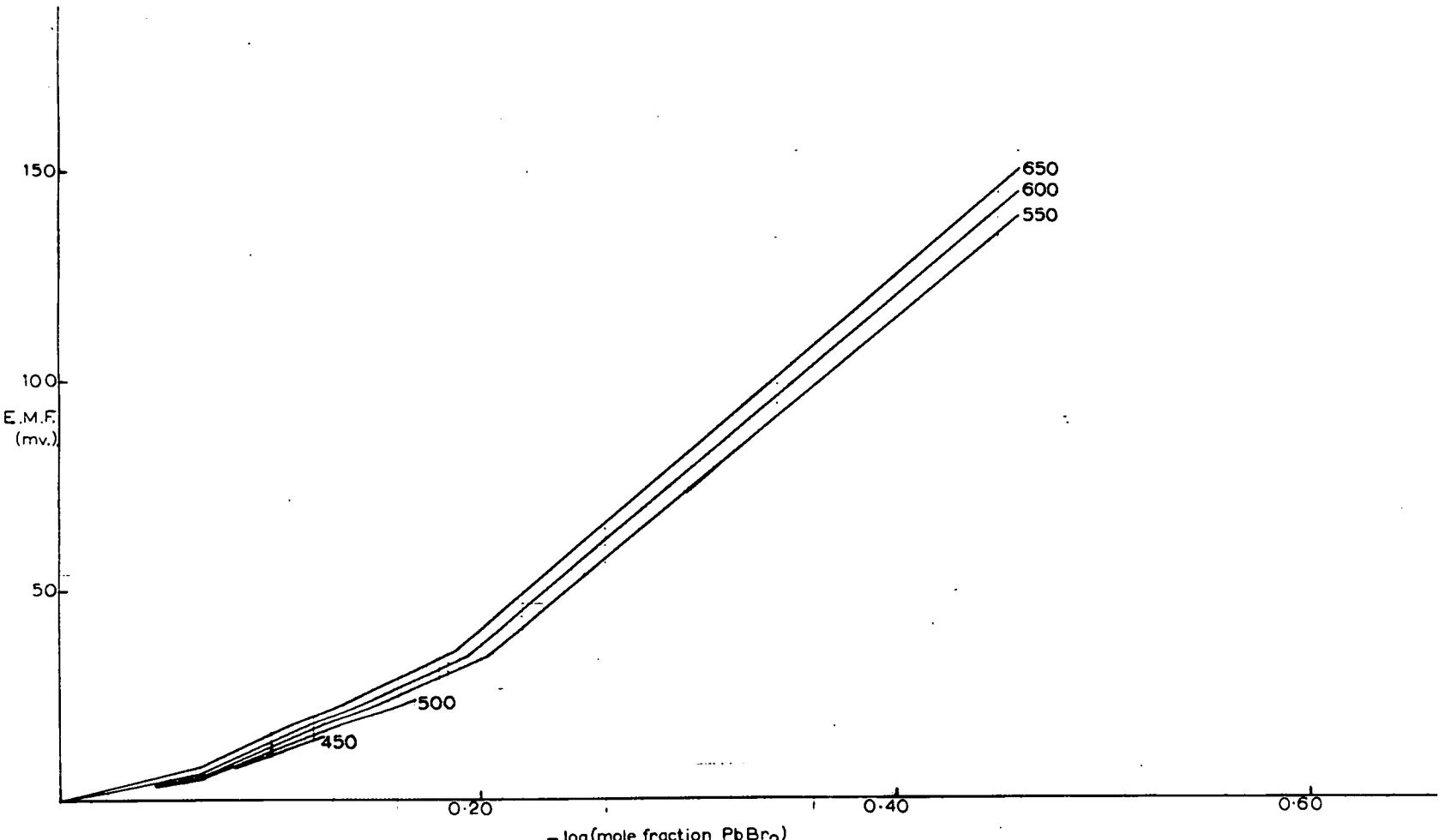

150
100
50
E.M.F. (mv.)
650
600
550
500
450
0·20
0·40
0·60
– log(mole fraction $PbBr_2$)

FIGURE 13(ii)

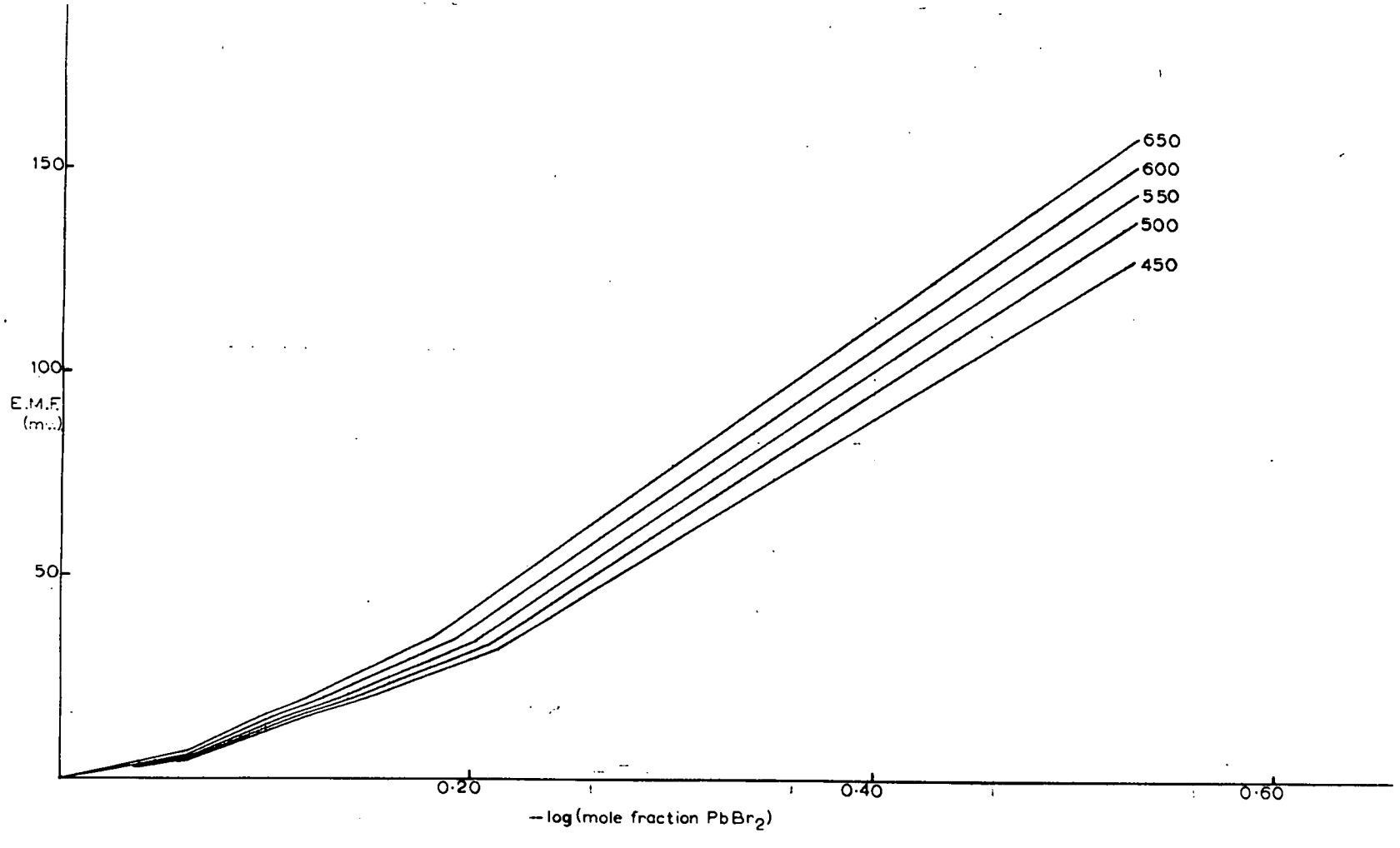

150
100
50
E.M.F
(m..)
650
600
550
500
450
0·20
0·40
0·60
— log (mole fraction $PbBr_2$)

FIGURE 13(iii)

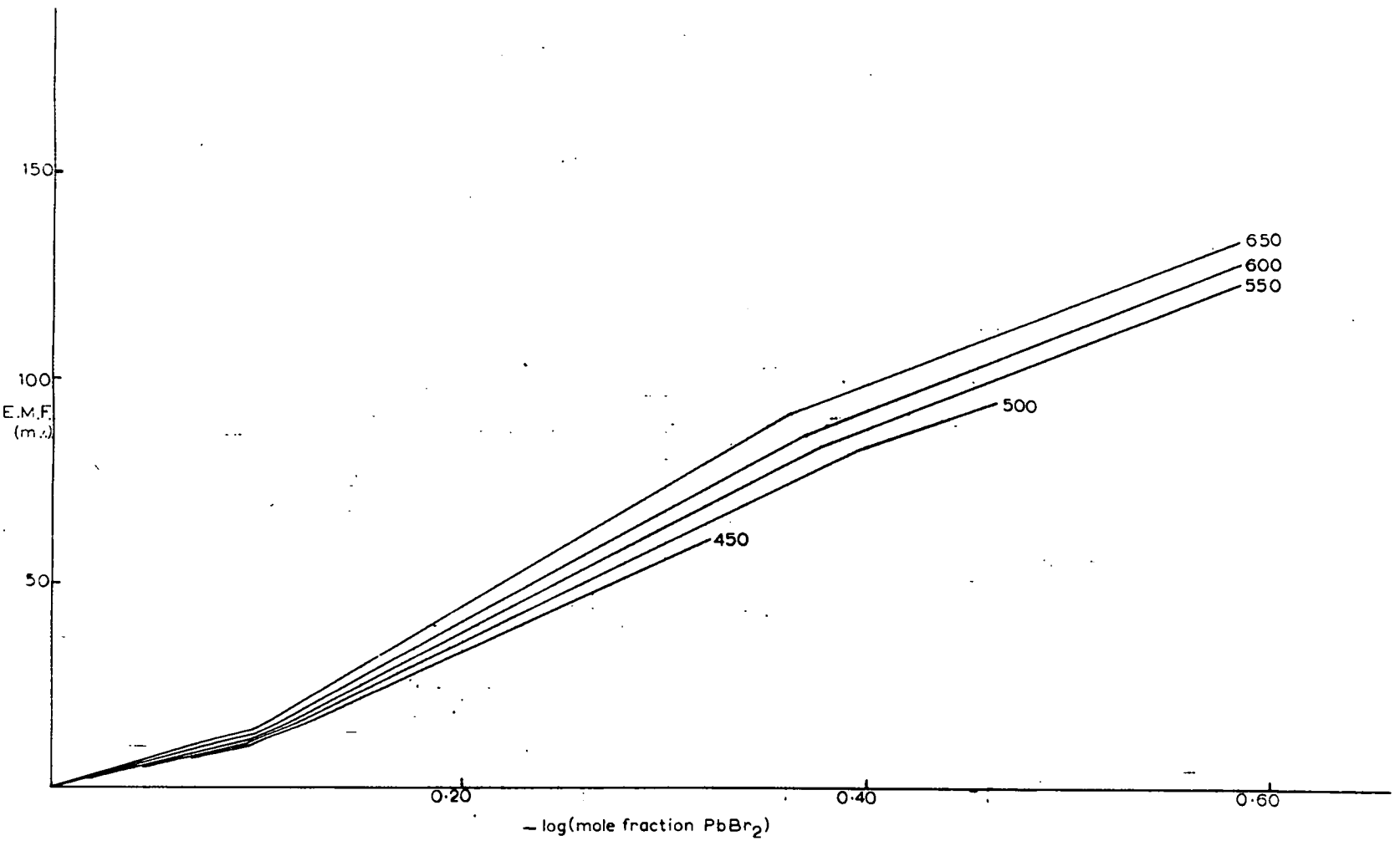


FIGURE 13 (iv)

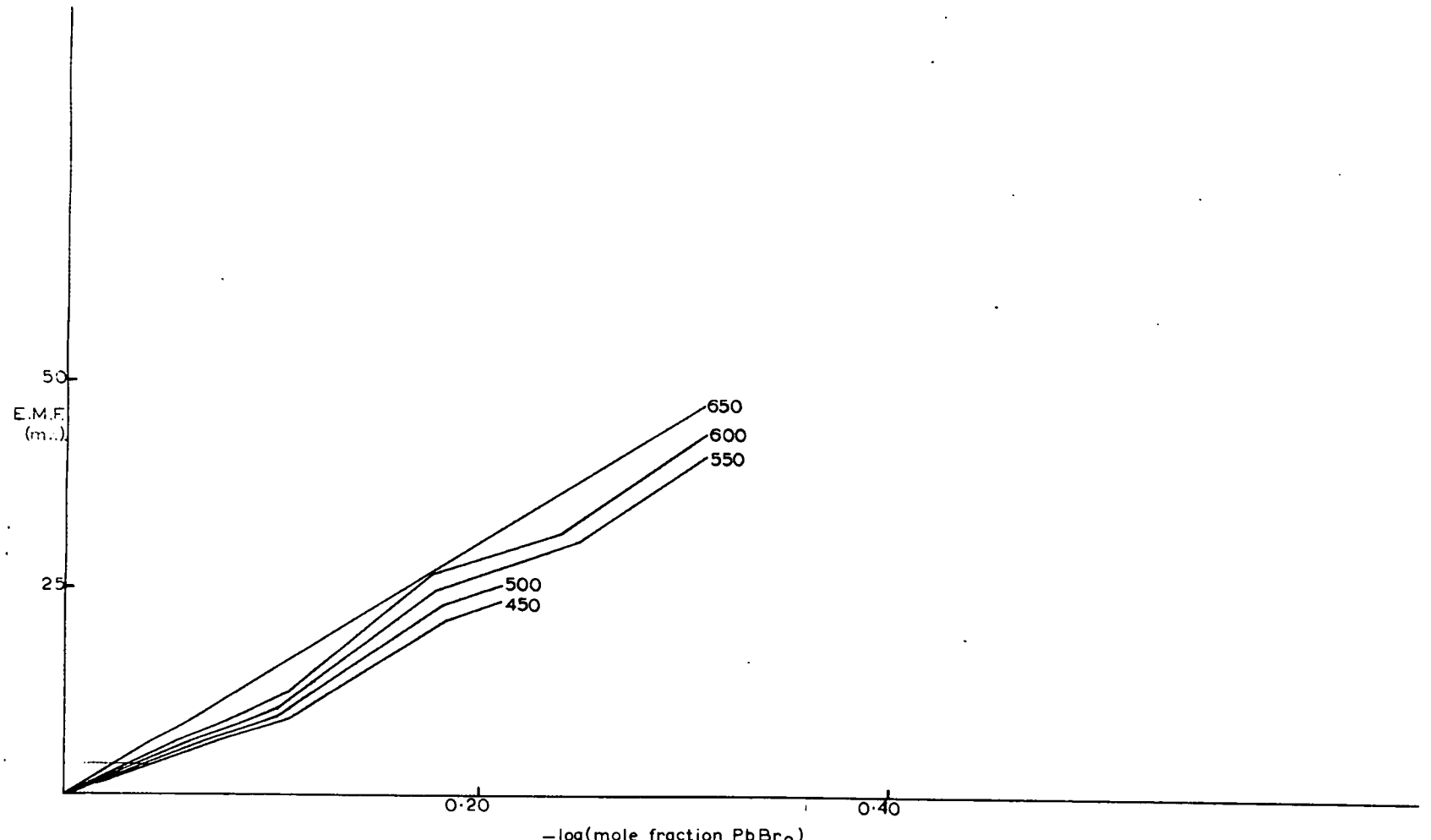

50
E.M.F.
(m.v.)
25
650
600
550
500
450
0·20
0·40
−log(mole fraction $PbBr_2$)

FIGURE 14

Plot of E.M.F. of concentration cells with transference against the negative logarithm of the mole fraction of lead halide, for chloride systems.

(i) $PbCl_2$ - CsCl

(ii) $PbCl_2$ - RbCl

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 14 (i)

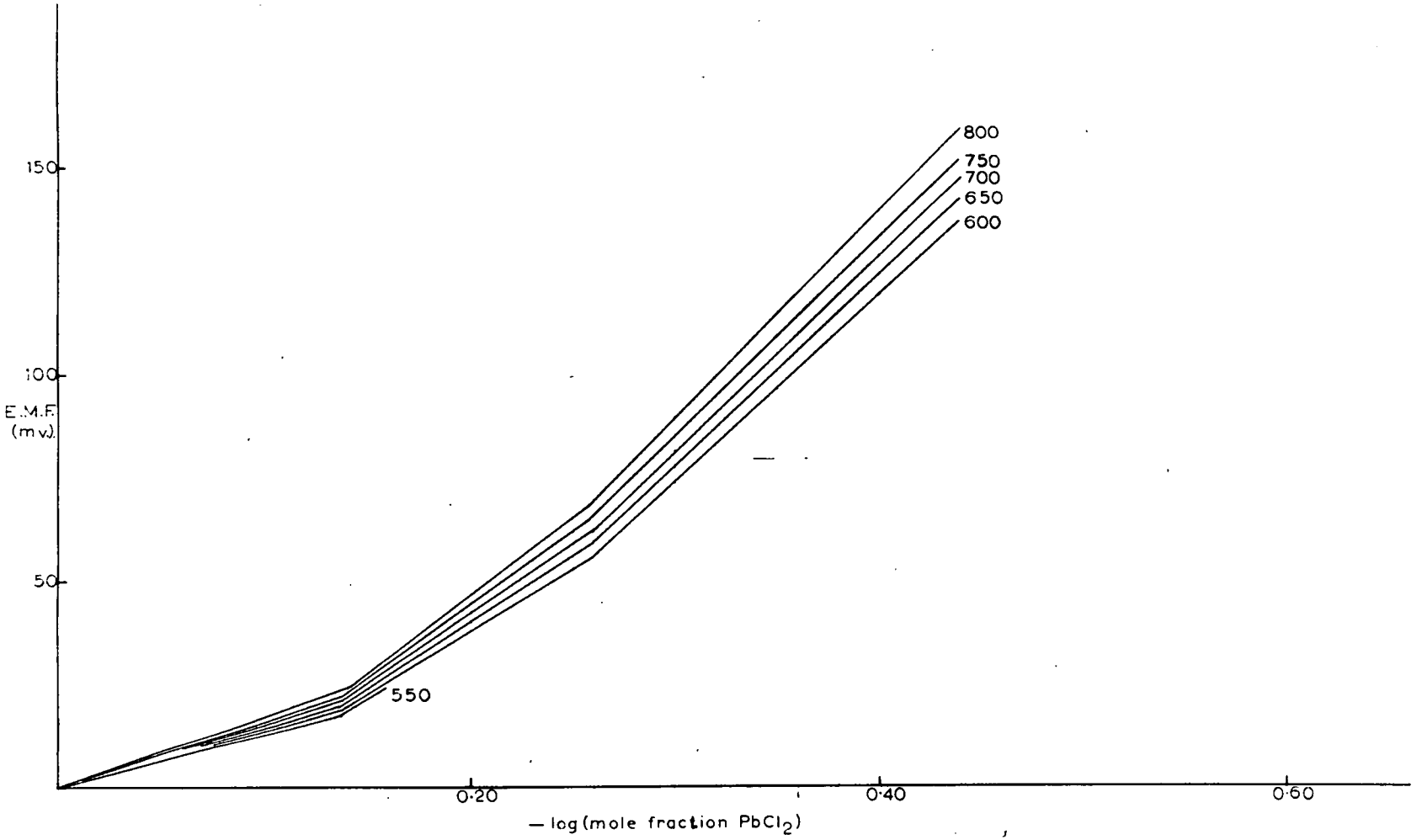

150
100
50
E.M.F. (mv.)
800
750
700
650
600
550
0·20
0·40
0·60
— log (mole fraction $PbCl_2$)

FIGURE 14(ii)

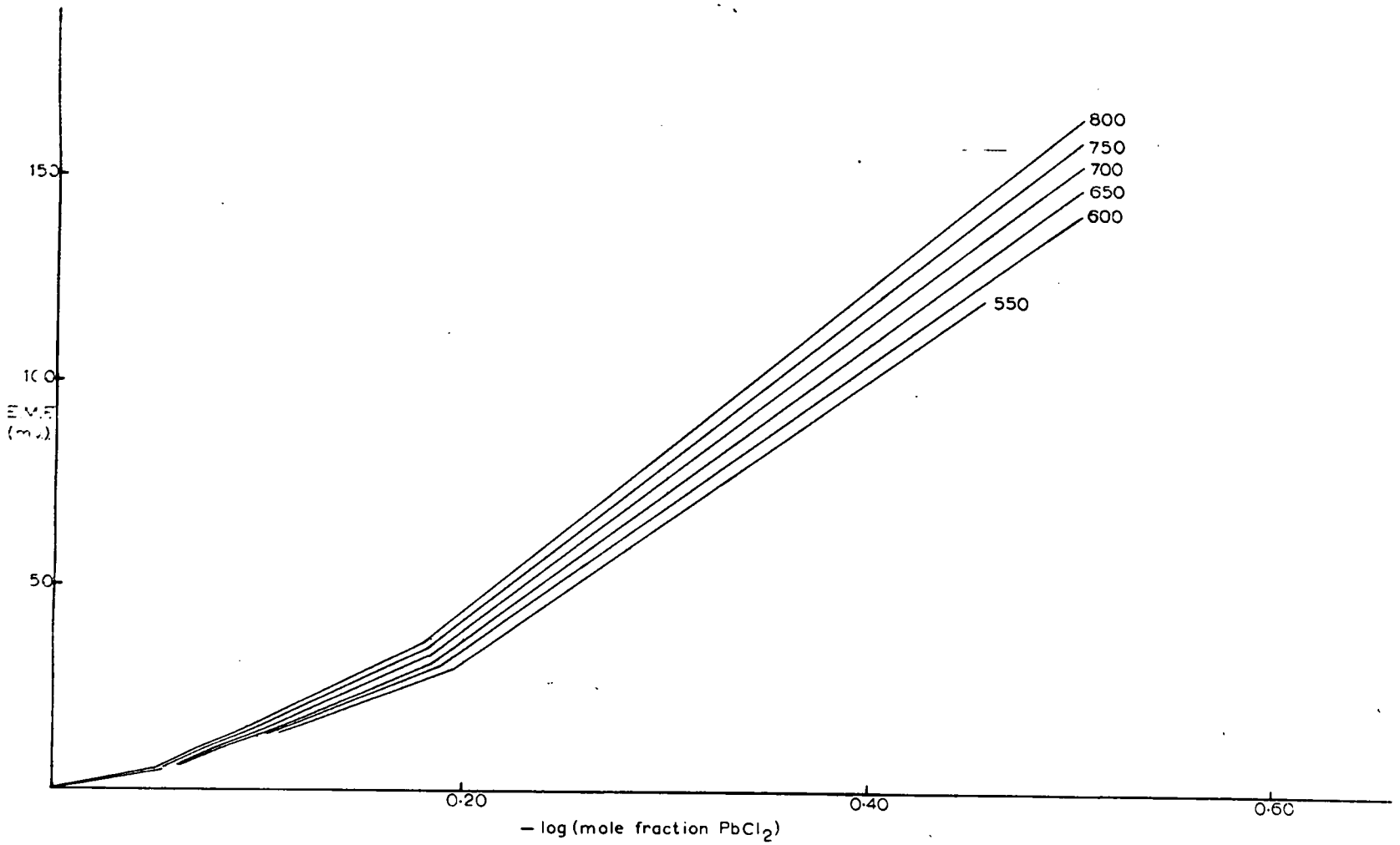

800
750
700
650
600
550
150
100
50
0·20
0·40
0·60
— log (mole fraction $PbCl_2$)

Table 3 (i) : System $PbBr_2$ - CsBr

T	E.M.F. / ($-\log x_{PbBr_2}$) relationships	x_c
450	$E_t = 0.000 + 65.217\,P$, (0.0000-0.052); $E_t = -5.476 + 163.450P$, (0.052-0.1249).	0.977
500	$E_t = 0.000 + 74.074\,P$, (0.0000-0.061); $E_t = -6.874 + 186.700P$, (0.061-0.1549).	0.937
550	$E_t = 0.000 + 83.333P$, (0.0000-0.067), $E_t = -8.420 + 211.164P$, (0.067-0.2007); $E_t = -48.160 + 409.215P$, (0.2007 - 0.4498).	0.970, 0.630
600	$E_t = 0.000 + 92.593P$, (0.0000-0.066); $E_t = -8.646 + 223.013P$, (0.066 - 0.1942); $E_t = -47.085 + 420.922P$, (0.1942 - 0.4498).	0.970, 0.640
650	$E_t = 0.000 + 116.667P$, (0.0000- 0.067); $E_t = -7.987 + 232.681P$, (0.067 - 0.1886); $E_t = -44.510 + 426.344P$, (0.1886 - 0.4498).	0.970, 0.648

Table 3. (ii) : System $PbBr_2$ - RbBr

T	E.M.F. / ($-\log x_{PbBr_2}$) relationships	x_c
450	$E_t = 0.000 + 68.986P$, (0.0000-0.059), $E_t = -6.986 + 183.440P$, (0.059 -0.2146), $E_t = -34.994 + 313.975P$, (0.2146-0.5229).	0.973, 0.610
500	$E_t = 0.000 + 78.431P$, (0.000-0.060), $E_t = -7.449 + 196.490P$, (0.060 - 0.2116), $E_t = -36.067 + 331.753P$, (0.2116 - 0.5229).	0.973, 0.614
550	$E_t = 0.000 + 83.333\,P$, (0.000-0.060); $E_t = -7.911 + 209.541P$, (0.060 - 0.2032), $E_t = -34.839 + 342.041P$, (0.2032 - 0.5229).	0.973, 0.626
600	$E_t = 0.000 + 95.238\,P$, (0.000 - 0.060); $E_t = -8.261 + 224.076P$, (0.060 - 0.1937), $E_t = -32.873 + 351.110P$, (0.1937 - 0.5229).	0.973, 0.640
650	$E_t = 0.000 + 100.000P$, (0.000 - 0.060); $E_t = -8.369 + 239.821P$, (0.060 - 0.1820), $E_t = -30.078 + 359.102P$, (0.1820 - 0.5229).	0.973, 0.658

Table 3. (iii) : System $PbBr_2$ - KBr.

T	E.M.F. / ($-\log x_{PbBr_2}$) relationships	x_c
450	$E_t = 0.000 + 102.273P$, (0.0000 - 0.095), $E_t = -11.969 + 228.848P$, (0.095-0.3325) .	0.804
500	$E_t = 0.000 + 111.111P$, (0.0000 - 0.095), $E_t = -12.738 + 244.620P$, (0.095-0.3947); $E_t = 16.278 + 171.122P$, (0.3947 - 0.4401).	0.804,0.403
550	$E_t = 0.000 + 119.565P$, (0.0000 - 0.096); $E_t = -13.318+259.505P$, (0.096 - 0.3763); $E_t = 9.700 + 198.342P$, (0.3763 - 0.5719).	0.802,0.421
600	$E_t = 0.000 + 132.653P$, (0.0000 - 0.098); $E_t = -13.766 + 273.965P$, (0.098 - 0.3730); $E_t = 14.786 + 197.433P$, (0.3730 - 0.5719).	0.798,0.424
650	$E_t = 0.000 + 146.341P$, (0.0000 - 0.098); $E_t = -14.424 + 295.783P$, (0.098 - 0.3637) $E_t = 22.083 + 195.417P$, (0.3637 - 0.5719).	0.798,0.433

Table 3. (iv) : System $PbBr_2$ - NaBr

T	E.M.F. / ($-\log x_{PbBr_2}$) relationships	x_c
450	$E_t = 0.000 + 75.000P$, (0.0000 - 0.092); $E_t = -7.260 + 155.776P$, (0.092 - 0.1776); $E_t = 4.975 + 88.889P$, (0.1776 - 0.2097).	0.809,0.664
500	$E_t = 0.000 + 91.463P$, (0.0000 - 0.098); $E_t = -7.830+ 171.258P$, (0.098 - 0.1808); $E_t = 7.770 + 85.000P$, (0.1808 - 0.2097).	0.798, 0.660
550	$E_t = 0.000 + 103.261P$, (0.0000 - 0.102); $E_t = -8.360 + 186.196 P$, (0.102-0.1801); $E_t = 10.566 + 81.111P$, (0.1801 - 0.2448); $E_t = -10.975+169.081P$, (0.2448-0.3325).	0.791, 0.661 0.569
600	$E_t = 0.000 + 117.925P$, (0.0000 - 0.107); $E_t = -9.246 + 204.880P$, (0.107-0.1771); $E_t = 13.362 + 77.222P$, (0.1771 - 0.2395); $E_t = -10.482 + 176.739P$, (0.2395-0.3325).	0.782,0.661, 0.569
650	$E_t = -0.253 + 155.349P$, (0.0223 - 0.3325).	

Table 4. (i) System $PbCl_2$ - CsCl

T	E.M.F. / (-log x_{PbCl_2}) relationships	x_c
550	E_t = 0.000 + 95.000P, (0.0000-0.137); E_t = -23.908+ 306.195P, (0.137-0.1593);	0.730.
600	E_t = 0.000 +103.175P, (0.0000-0.138); E_t = -22.339+ 302.410P, (0.138-0.2615); E_t = -62.742+ 456.918P, (0.2615 - 0.4597).	0.728, 0.548
650	E_t = 0.000 + 108.333P, (0.0000 - 0.136); E_t = -23.739+ 319.902P, (0.136-0.2604); E_t = -62.066 + 467.073P, (0.2604 - 0.4597).	0.731, 0.549
700	E_t = 0.000 + 116.071P, (0.0000 - 0.137), E_t = -25.116 + 337.650P, (0.137-0.2593); E_t = -60.956 + 475.853P, (0.2593 - 0.4597).	0.730, 0.550
750	E_t = 0.000 + 127.451P, (0.0000 - 0.138); E_t = -26.345 + 354.124P, (0.138-0.2554); E_t = -59.185 + 482.710P, (0.2554 - 0.4597).	0.728, 0.555
800	E_t = 0.000 + 138.298P, (0.0000 - 0.141); E_t = -28.209 + 375.225P, (0.141 - 0.2555); E_t = -61.224 + 504.451P, (0.2555 - 0.4597).	0.723, 0.555

Table 4. (ii) : System $PbCl_2$ - RbCl

T	E.M.F. / (-log x_{PbCl_2}) relationships	X_c
550	E_t = 0.000 + 79.167P, (0.0000 - 0.060); E_t = -6.465 + 187.640P, (0.060 - 0.1952); E_t = -38.273 + 350.627P, (0.1952 - 0.4559).	0.871, 0.638
600	E_t = 0.000 + 83.333P, (0.0000 - 0.059); E_t = -6.910 + 199.473P, (0.059-0.1881); E_t = -36.579 + 357.212P, (0.1881 - 0.5031).	0.873, 0.649
650	E_t = 0.000 + 86.207P, (0.0000 - 0.058); E_t = -7.274 + 210.551P, (0.058 - 0.1845); E_t = -36.412 + 368.457P, (0.1845 - 0.5031).	0.875, 0.654
700	E_t = 0.000 + 89.286P, (0.0000 - 0.057); E_t = -7.633 + 223.356P, (0.057 - 0.1832); E_t = -36.425 + 380.526P, (0.1832 - 0.5031).	0.877, 0.656
750	E_t = 0.000 + 94.340P, (0.0000 - 0.053); E_t = -7.399 + 232.664P, (0.053 - 0.1798); E_t = -35.734 + 390.261P, (0.1798 - 0.5031).	0.885, 0.661
800	E_t = 0.000 + 96.154 P, (0.0000 - 0.050); E_t = -7.545 + 243.821P, (0.050 - 0.1805); E_t = -36.414 + 403.750P, (0.1805 - 0.5031).	0.891, 0.660.

2. Diffusion Potential

Values of the diffusion potential, ε , were obtained as follows: The E.M.F's of the concentration cells without transference[1-3] corresponding to the concentration cells with transference investigated here, were plotted against mole fraction of alkali halide, at various temperatures. The curves were then interpolated to give values of the E.M.F. at the same compositions as those at which experimental values of E.M.F. were measured in this work. By subtraction of E (E.M.F. of the cell without transference) from E_t (E.M.F. of the corresponding cell with transference), the values of diffusion potential, for various compositions and temperatures, were deduced.

In the case of the system $PbBr_2$ - NaBr, the data for the cell without transference was known at only one temperature, and hence the value of the diffusion potential could be calculated at only one temperature.

The diffusion potential data obtained is tabulated below (Tables 5, (i) to (iv) and Tables 6, (i) and (ii)). In these Tables, the units of diffusion potential are millivolts, T is the temperature (^oC) and x_{PbX_2} is the mole fraction of PbX_2 in the bulk electrolyte. All unsigned values of diffusion potential are positive values.

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1. Lantratov and Shevlyakova, Zh.Neorgan.Khim., 6 , 95 (1961)(System $PbBr_2$ - NaBr)
2. Markov, Delimarskii and Panchenko, Zh.Fiz.Khim., 28, 1987 (1954) (System $PbCl_2$ - RbCl)
3. White, to be published. (Systems $PbBr_2$ - CsBr, - RbBr and -KBr; $PbCl_2$ - CsCl).

Table 5. (i) : values of the diffusion potential in the System $PbBr_2$ - CsBr.

x_{PbBr_2} \ T	450	500	550	600	650
0.949	1.3	1.2	1.1	1.9	1.3
0.888	3.5	2.9	2.5	2.0	2.3
0.845	5.6	4.8	4.1	3.5	3.3
0.798	6.8	5.8	5.2	4.2	4.0
0.750	4.6	3.8	3.1	2.5	2.2
0.700		4.0	3.8	3.8	4.4
0.654			5.5	5.5	4.6
0.603			8.7	8.8	9.4
0.550			15.9	16.5	16.7
0.510			25.6	26.9	27.0
0.454			23.4	25.1	26.0
0.408			27.8	28.8	29.2
0.355			31.0	31.4	30.4

Table 5. (ii) : values of the diffusion potential in the System $PbBr_2$ - RbBr.

x_{PbBr_2} \ T	450	500	550	600	650
0.942	-1.0	-0.8	-0.6	-0.5	-0.3
0.899	-0.3	0.0	0.5	0.8	2.1
0.842	-0.7	-0.2	0.2	0.7	1.7
0.800	0.1	0.7	1.2	1.8	3.0
0.744	0.1	0.8	1.6	2.5	3.9
0.694	1.5	2.7	3.6	5.2	7.3
0.646	3.2	4.5	5.7	7.0	9.7
0.597	3.8	5.3	6.8	8.6	11.2
0.546	3.4	5.2	7.5	11.1	13.1
0.500	4.2	7.1	10.1	13.0	16.2
0.444	5.4	8.3	12.1	14.8	19.2
0.398	10.3	13.7	16.9	20.7	25.4
0.348	19.0	21.5	24.3	26.9	30.0
0.300		29.7	31.9	33.3	34.9

Table 5. (iii) : values of the diffusion potential in the System $PbBr_2$ - KBr.

x_{PbBr_2} \ T	450	500	550	600	650
0.911	-0.8	-0.2	0.2	1.1	1.9
0.854	-1.0	0.1	1.0	2.3	3.8
0.786	-0.2	1.3	2.8	4.7	6.3
0.770	1.7	3.3	5.1	7.2	8.9
0.718	3.1	5.4	7.7	10.3	14.2
0.655	7.5	10.0	13.5	17.0	21.7
0.592	10.6	14.2	17.9	21.8	27.0
0.565	8.8	12.8	18.4	21.4	27.5
0.532	10.5	15.4	20.8	26.0	33.2
0.465	-0.8	6.1	12.2	17.9	24.5
0.408	-1.4	4.1	9.4	14.4	21.1
0.363		5.1	8.9	12.4	18.8
0.318			11.9	13.6	18.4
0.268			21.9	21.4	23.9

Table 5. (iv) : values of the diffusion potential in the System $PbBr_2$ - NaBr.

x_{PbBr_2} \ T	589
0.950	0.7
0.899	1.5
0.863	1.3
0.780	2.2
0.754	2.7
0.705	4.6
0.683	6.5
0.630	5.5
0.617	4.9
0.546	3.1
0.500	7.1
0.465	4.5

Table 6. (i) : Values of the diffusion potential in the system $PbCl_2$ - CsCl

T / x_{PbCl_2}	550	600	650	700	750	800
0.908	-2.0	-1.3	-0.8	0.0	0.7	1.4
0.814	-0.6	-1.9	-2.6	-3.6	-4.1	-4.7
0.944	-0.7	-0.2	0.2	0.9	1.4	1.9
0.843	-1.3	-2.7	-3.5	-4.6	-5.8	-6.8
0.730	1.3	1.2	0.8	0.9	0.8	0.7
0.693		3.8	4.0	4.5	4.9	5.1
0.644		1.9	2.6	3.3	4.2	5.9
0.593		5.5	7.3	8.9	10.3	11.8
0.539		11.1	12.5	13.8	14.6	15.4
0.493		15.9	17.0	17.9	18.3	20.5
0.445		17.2	18.7	20.2	21.8	24.1
0.396		22.4	24.4	26.4	27.6	31.8
0.347		27.9	30.0	31.1	31.3	36.2

Table 6. (ii) : values of the diffusion potential in the system $PbCl_2$ - RbCl

T / x_{PbCl_2}	550	600	650	700	750	800
0.955	-1.7	-2.0	-2.2	-2.5	-2.8	-3.2
0.900	-1.9	-2.7	-3.1	-3.5	-3.8	-4.1
0.820	-4.2	-4.9	-5.5	-6.1	-6.7	-7.2
0.759	-1.8	-2.3	-2.8	-3.1	-3.2	-3.4
0.702	-1.9	-2.2	-2.7	-3.4	-4.4	-5.8
0.655	-2.2	-2.6	-3.8	-4.4	-4.6	-5.2
0.569	1.8	0.6	0.5	0.6	2.2	2.9
0.555	3.8	4.2	4.6	5.2	5.8	5.4
0.503	6.5	7.1	7.6	7.8	8.2	8.2
0.455	10.4	12.2	13.5	14.5	15.5	18.2
0.407	12.5	14.4	16.0	17.4	18.8	19.9
0.350	14.1					

(i) Composition Dependence of Diffusion Potential

The variation of diffusion potential with composition of the bulk electrolyte is illustrated graphically by the isotherms of Figures 15 (i) to (iv), 16 (i) and (ii), 17 (i) to (iv) and 18 (i) and (ii).

(ii) Temperature Dependence of Diffusion Potential

The variation of diffusion potential with temperature is shown in Figures 19 (i) to (iii), and Figures 20 (i) and (ii). For those systems which exhibited a linear dependence of diffusion potential on temperature for several compositions (namely, the systems $PbCl_2$ - CsCl, $PbCl_2$ - RbCl and $PbBr_2$ - RbBr), the equations to the lines of best fit were calculated for the points concerned, by the method of least squares. The equations are presented in Table 7. ($PbBr_2$ - RbBr), and Tables 8.(i) ($PbCl_2$ - CsCl) and 8. (ii) ($PbCl_2$ - RbCl). In some cases the points appeared to lie on two straight lines (with very small deviations from the lines), and in such cases they were assumed to do so, and treated accordingly.

In Tables 7 and 8, x_{PbX_2} is the mole fraction of PbX_2 in the bulk electrolyte, $\mathcal{E}$ is the diffusion potential (millivolts) and T is the temperature (^{o}C). T' denotes the temperatures at which changes in slope appear in the $\mathcal{E}$ / T lines. The figures in parentheses indicate the temperature range of applicability of the equations.

FIGURE 15.

Plot of diffusion potential against mole fraction of lead halide, for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr.

(iv) $PbBr_2$ - NaBr

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 15(1)

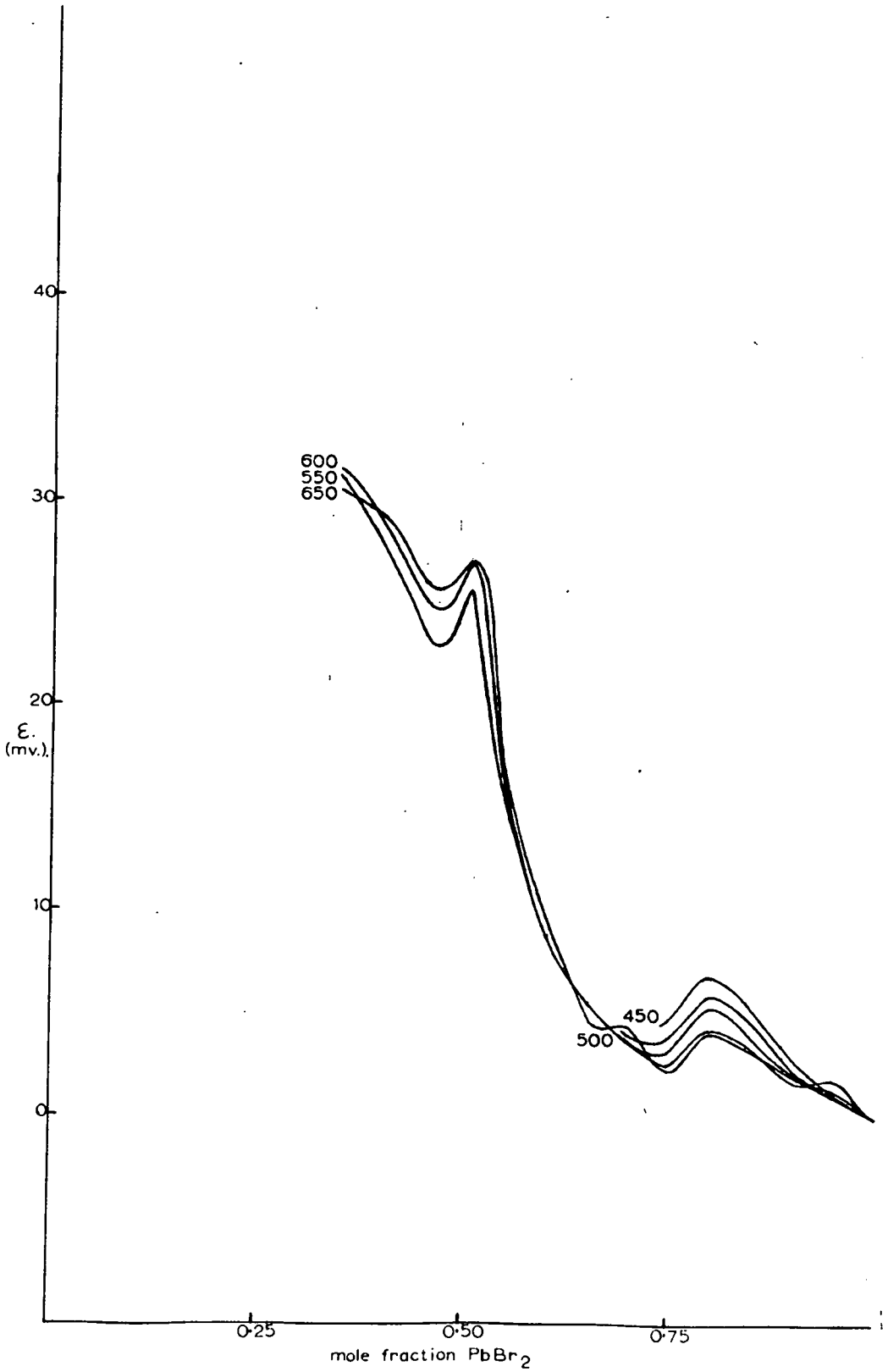
40
30
20
10
0
E.
(mv.)
600
550
650
450
500
0·25
0·50
0·75
mole fraction PbBr2

FIGURE 15(ii)

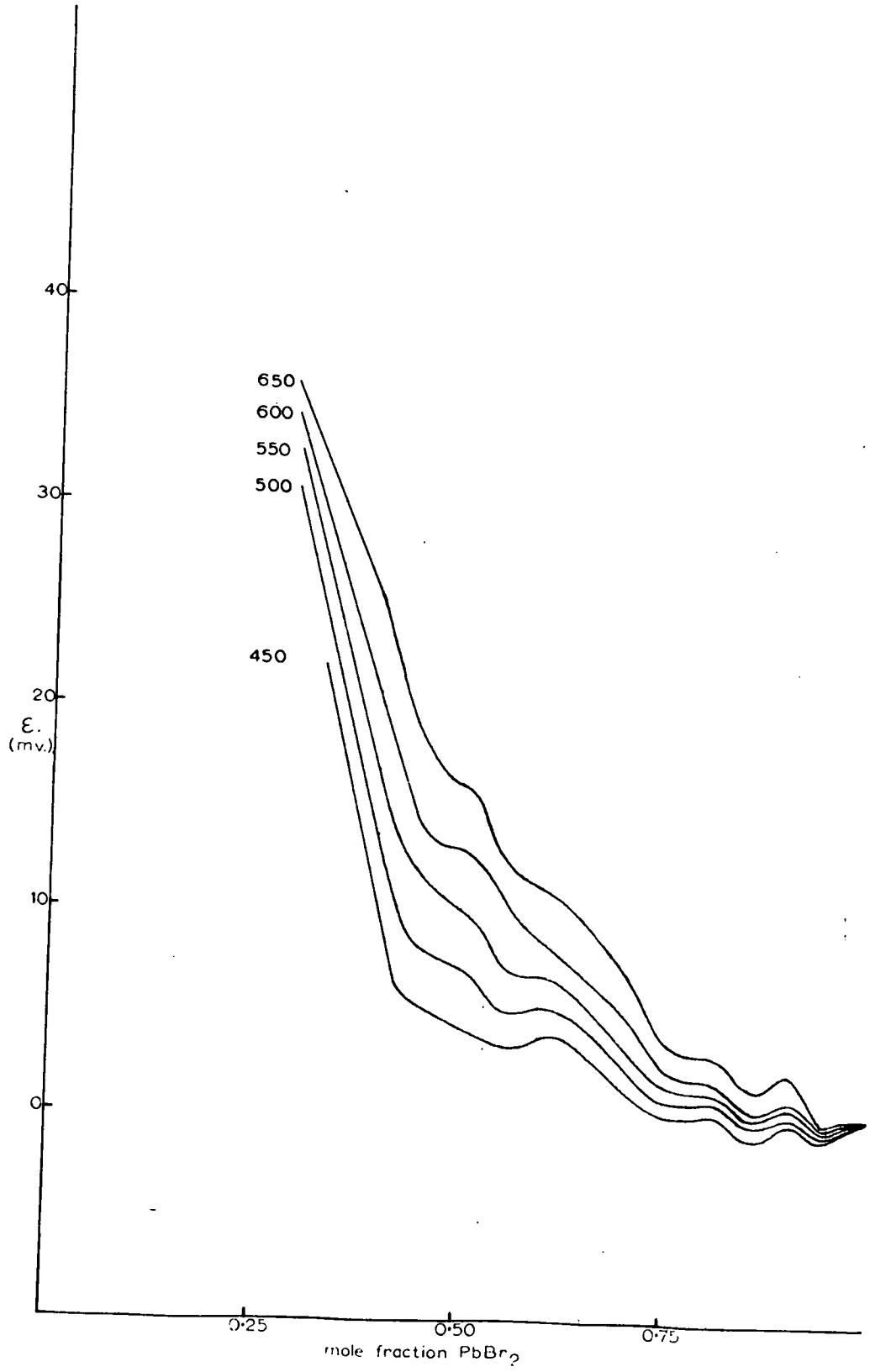
40
30
20
10
0
E.
(mv.)
650
600
550
500
450
0·25
0·50
0·75
mole fraction PbBr2

FIGURE 15(iii)

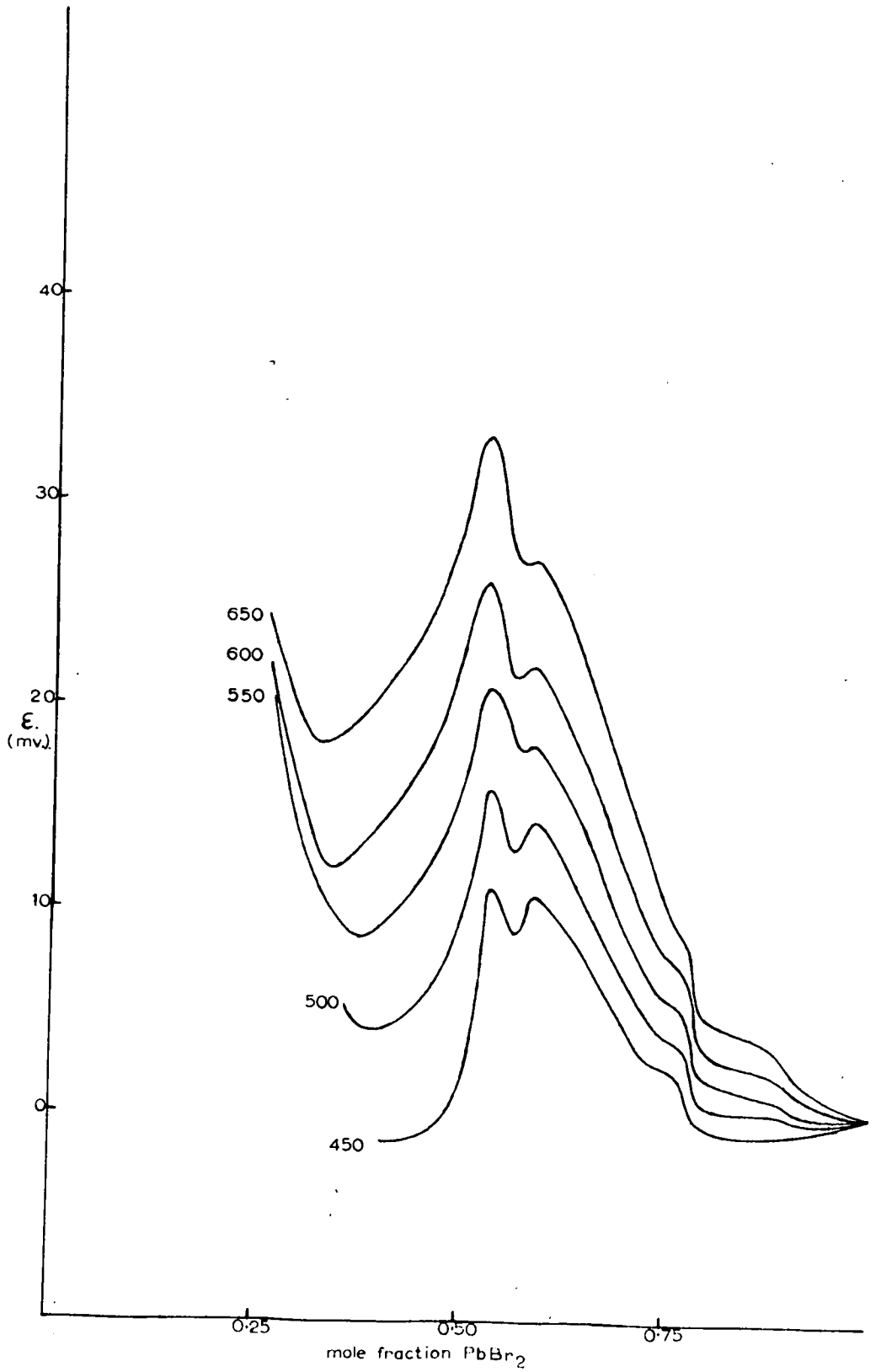

FIGURE 15(iv)

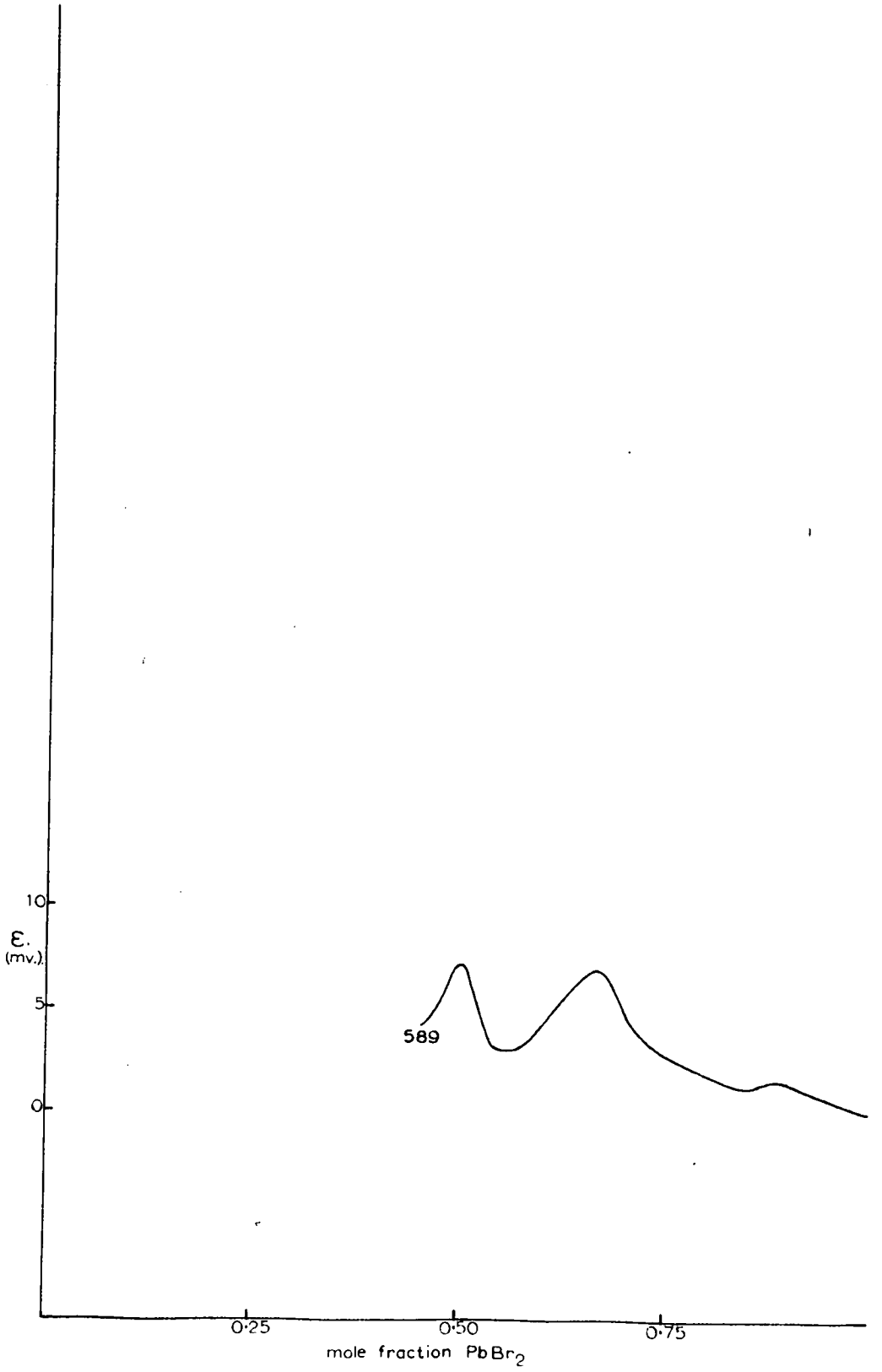

FIGURE 16

Plot of diffusion potential against mole fraction of lead halide, for chloride systems.

(i) $PbCl_2$ - CsCl

(ii) $PbCl_2$ - RbCl

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 16(i)

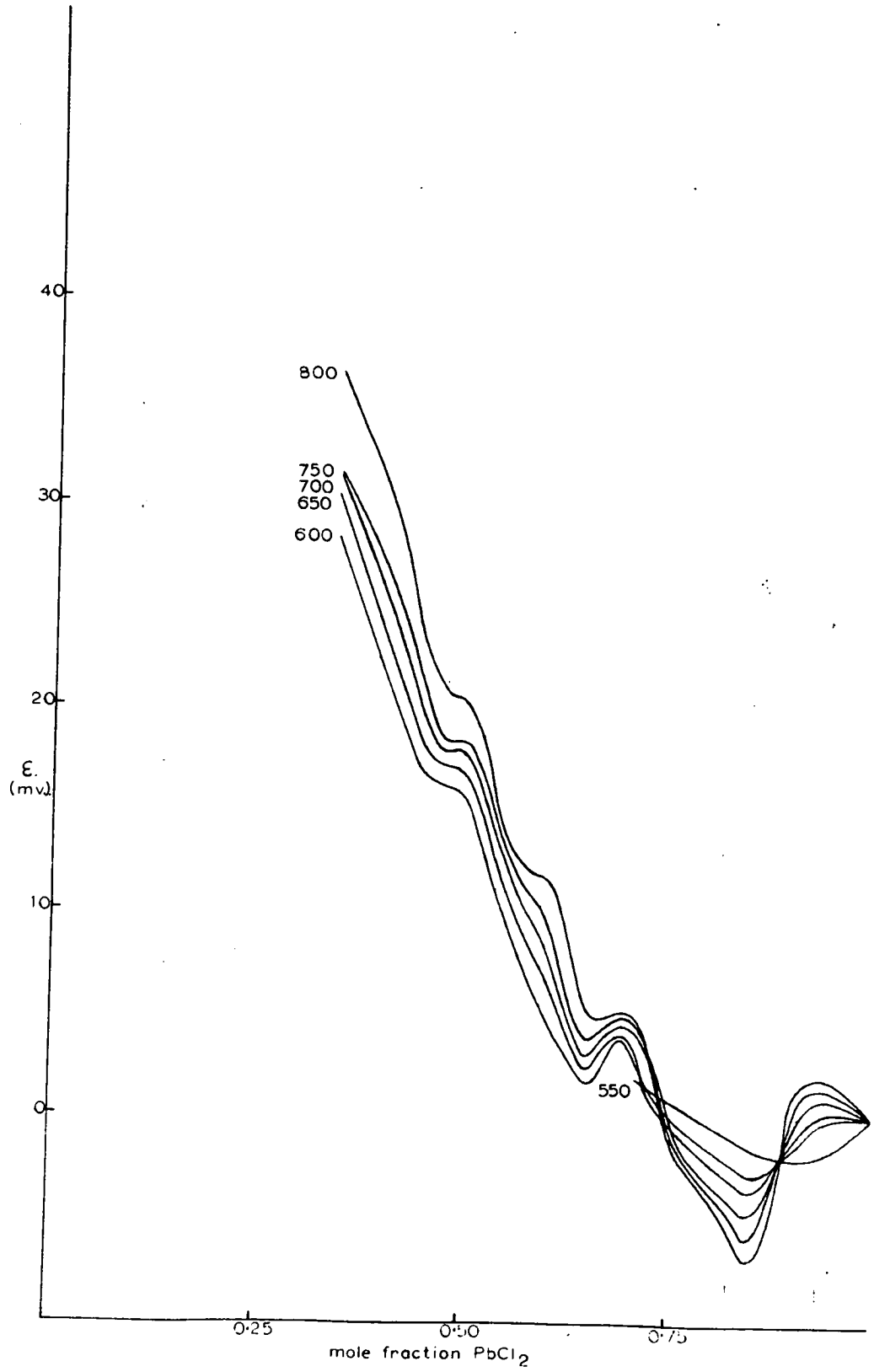
40
30
20
10
0
E.
(mv.)
800
750
700
650
600
550
0·25
0·50
0·75
mole fraction $PbCl_2$

FIGURE 16(ii)

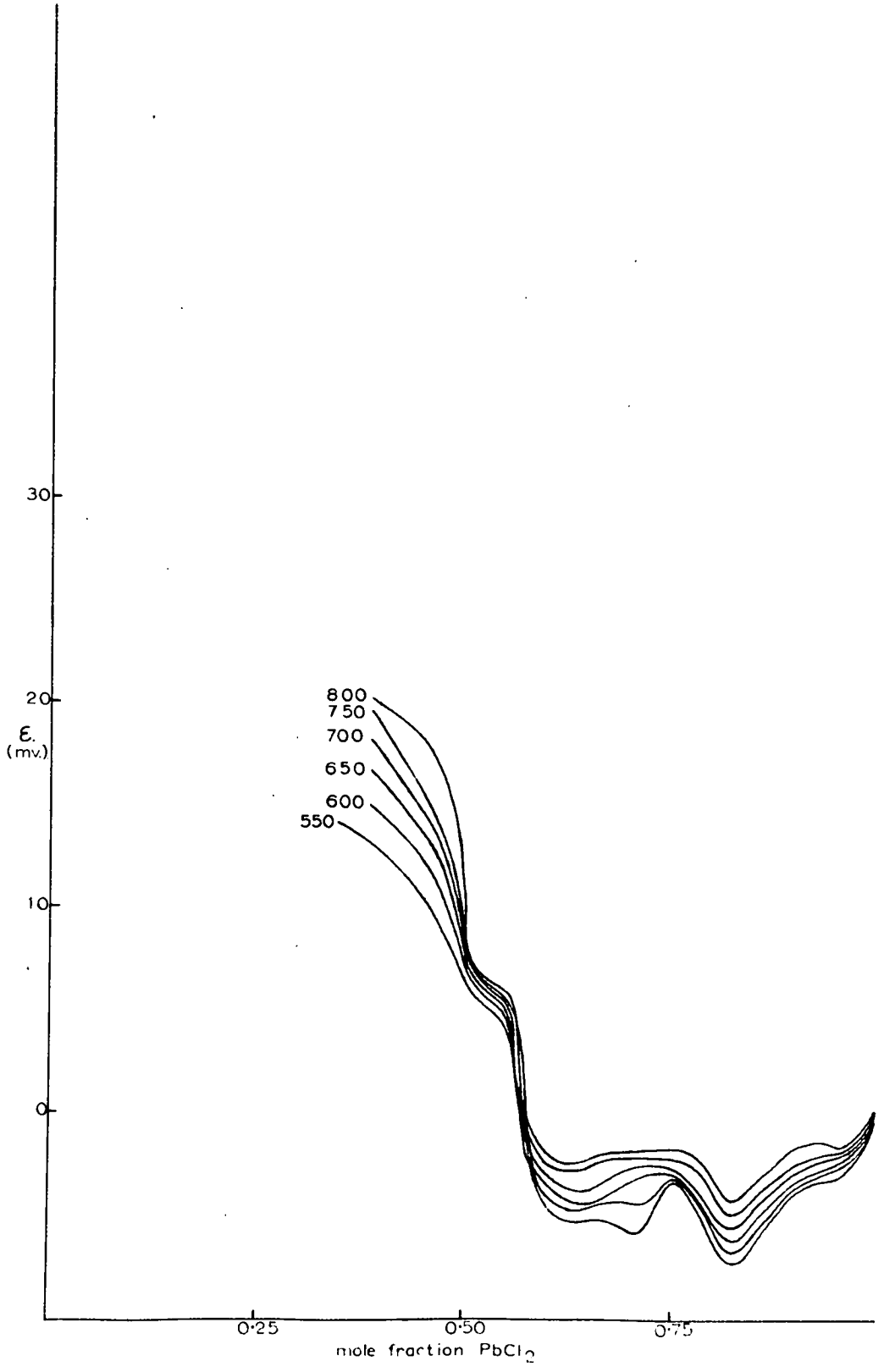
30
20
10
0
E.
(mv.)
800
750
700
650
600
550
0·25
0·50
0·75
mole fraction $PbCl_2$

FIGURE 17

Plot of diffusion potential against the negative logarithm of the mole fraction of lead halide, for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr

(iv) $PbBr_2$ - NaBr

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 17(i)

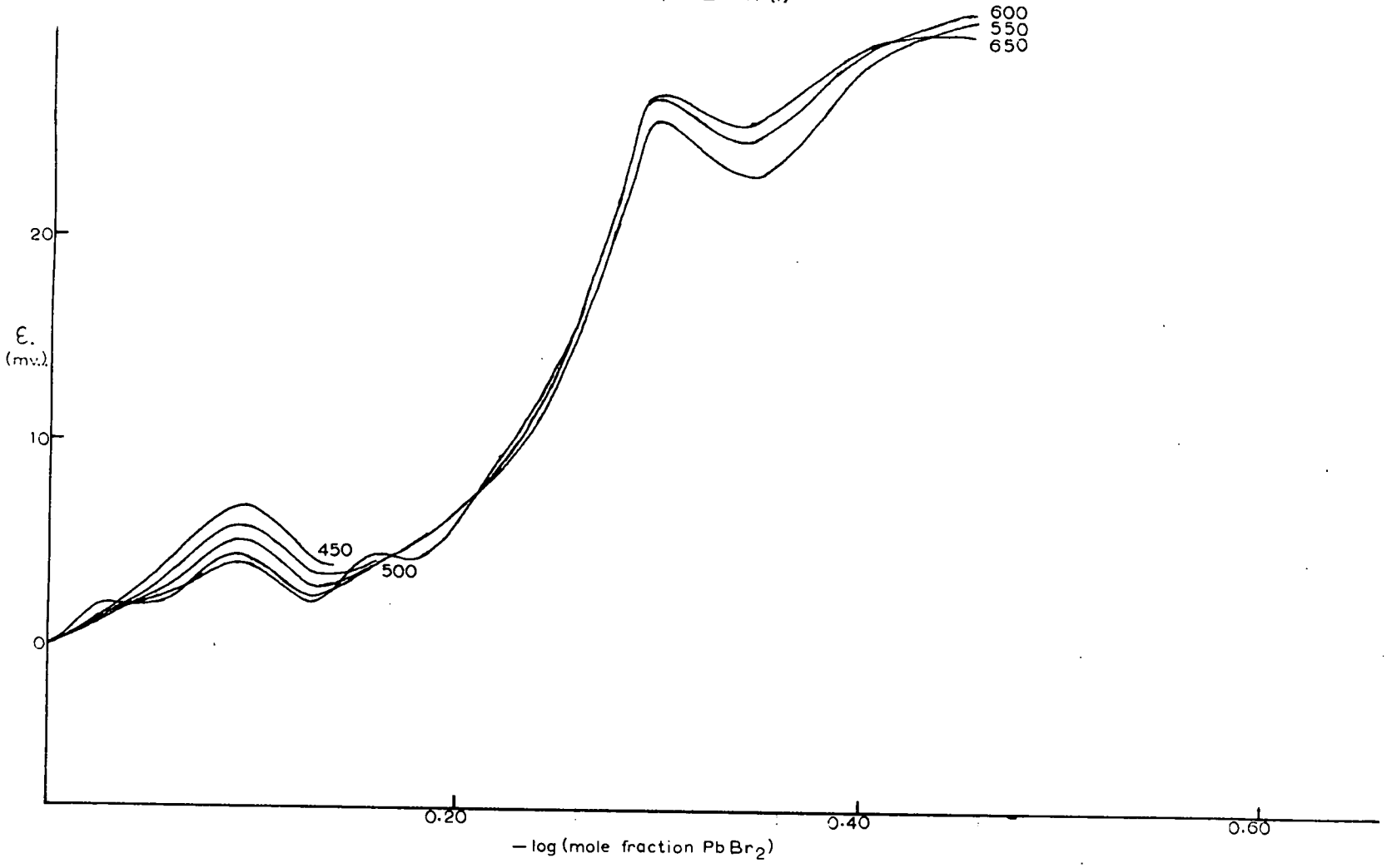
600
550
650
20
ε.
(mv.)
10
450
500
0
0.20
0.40
0.60
— log (mole fraction $PbBr_2$)

FIGURE 17(ii)

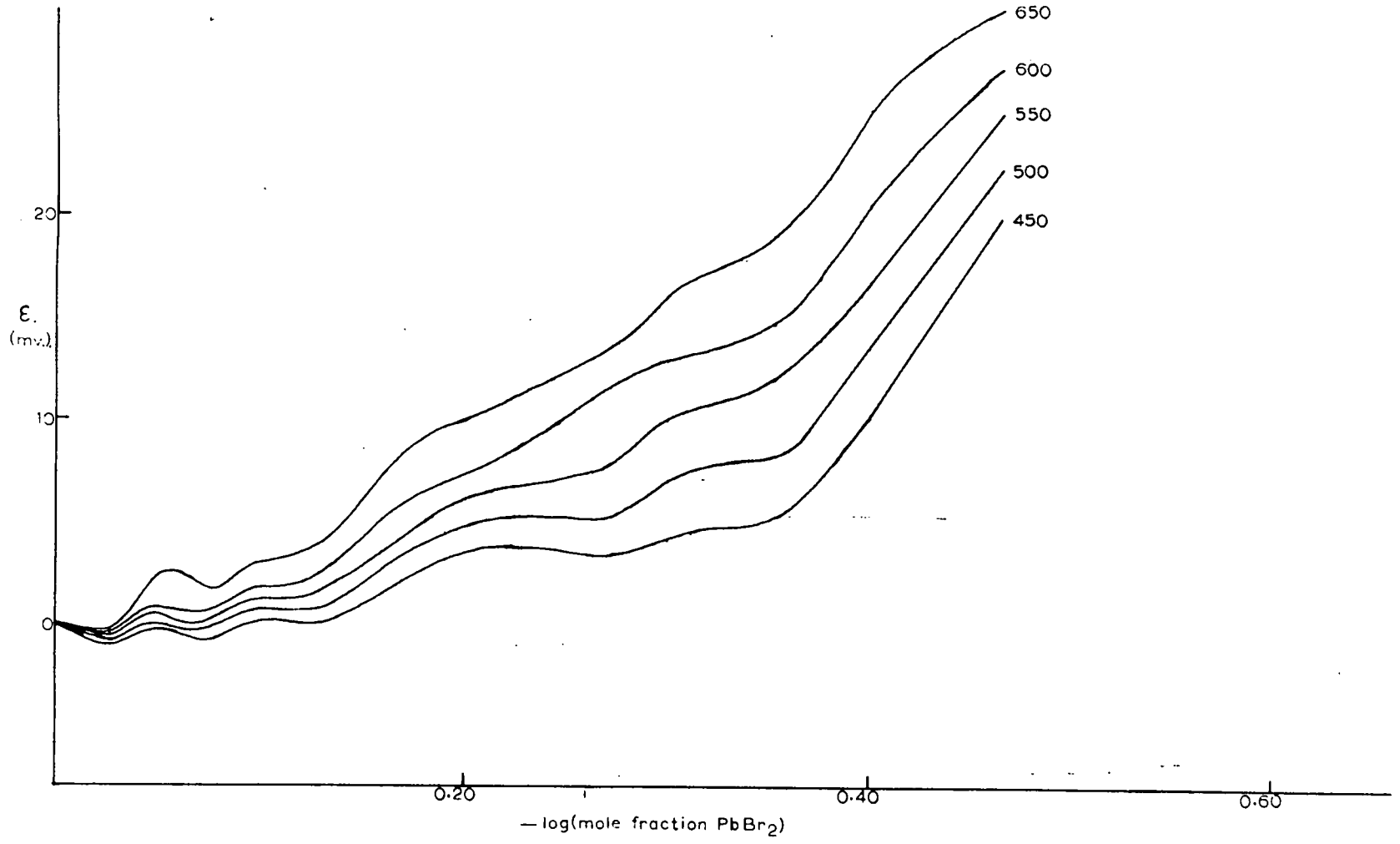
650
600
550
500
450
20
10
0
E.
(mv.)
0.20
0.40
0.60
— log(mole fraction PbBr2)

FIGURE 17(iii)

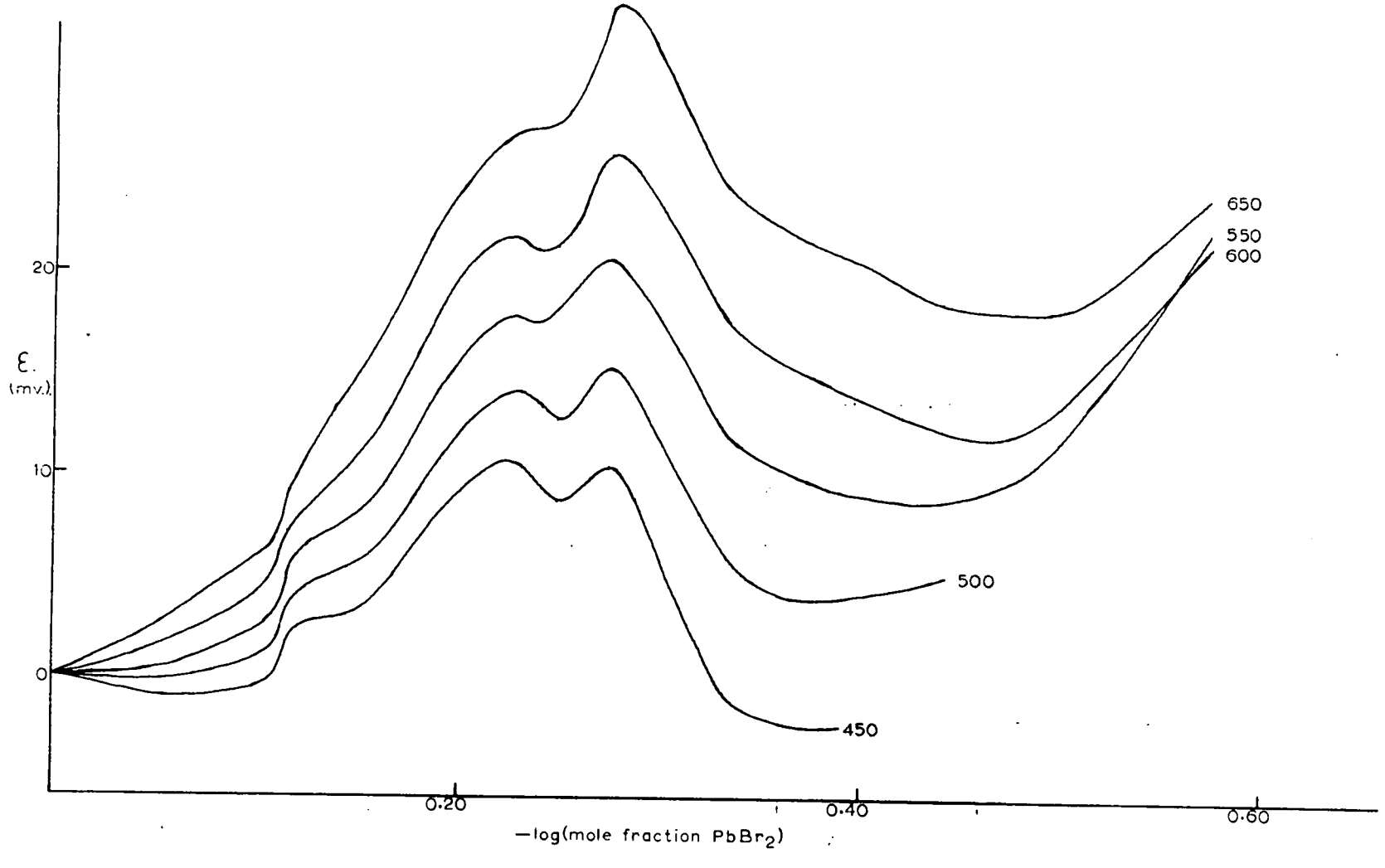

FIGURE 17(iv)

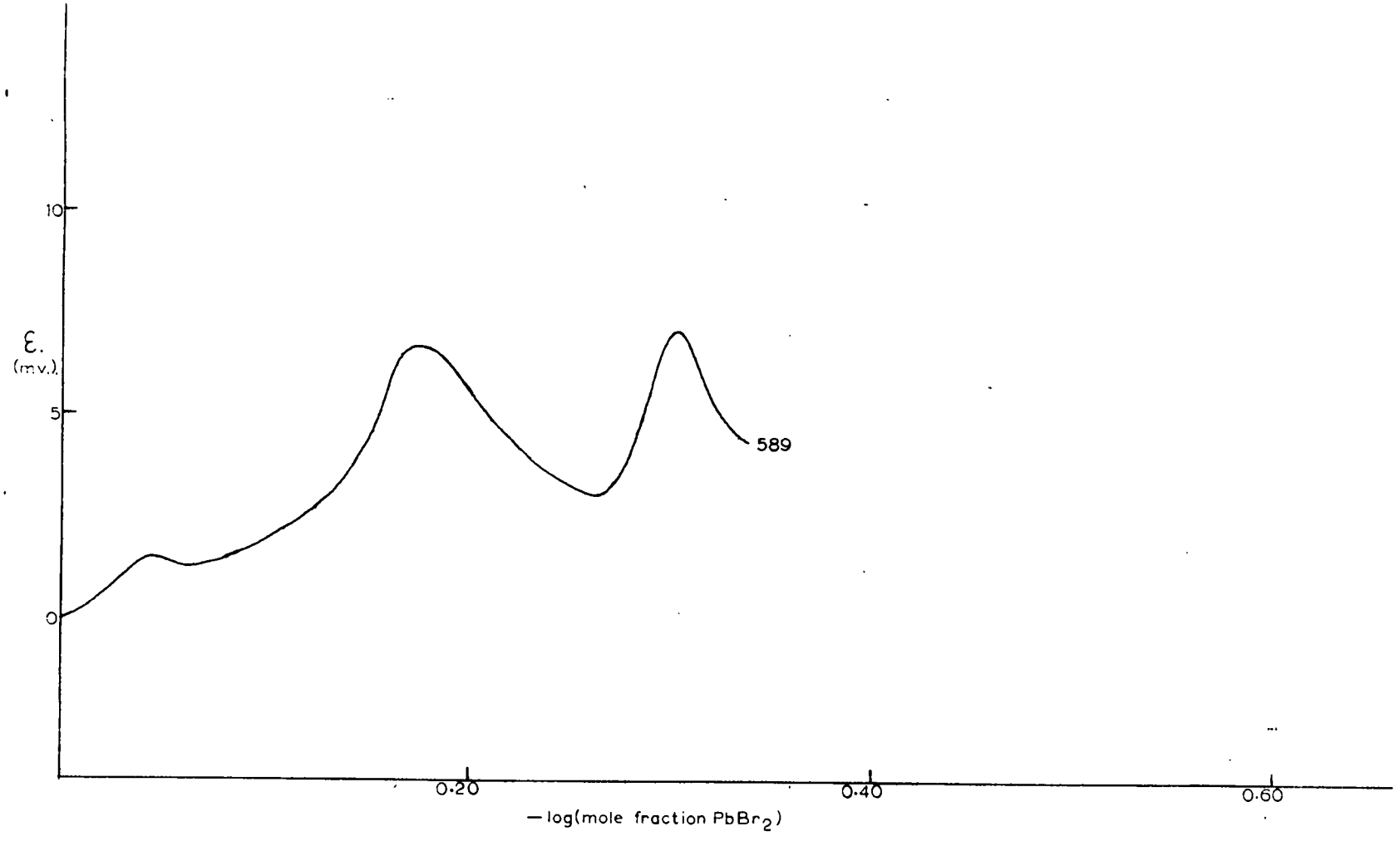

FIGURE 18

Plot of diffusion potential against the negative logarithmof the mole fraction of lead halide, for chloride systems.

(i) $PbCl_2$ - CsCl

(ii) $PbCl_2$ - RbCl

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 18(i)

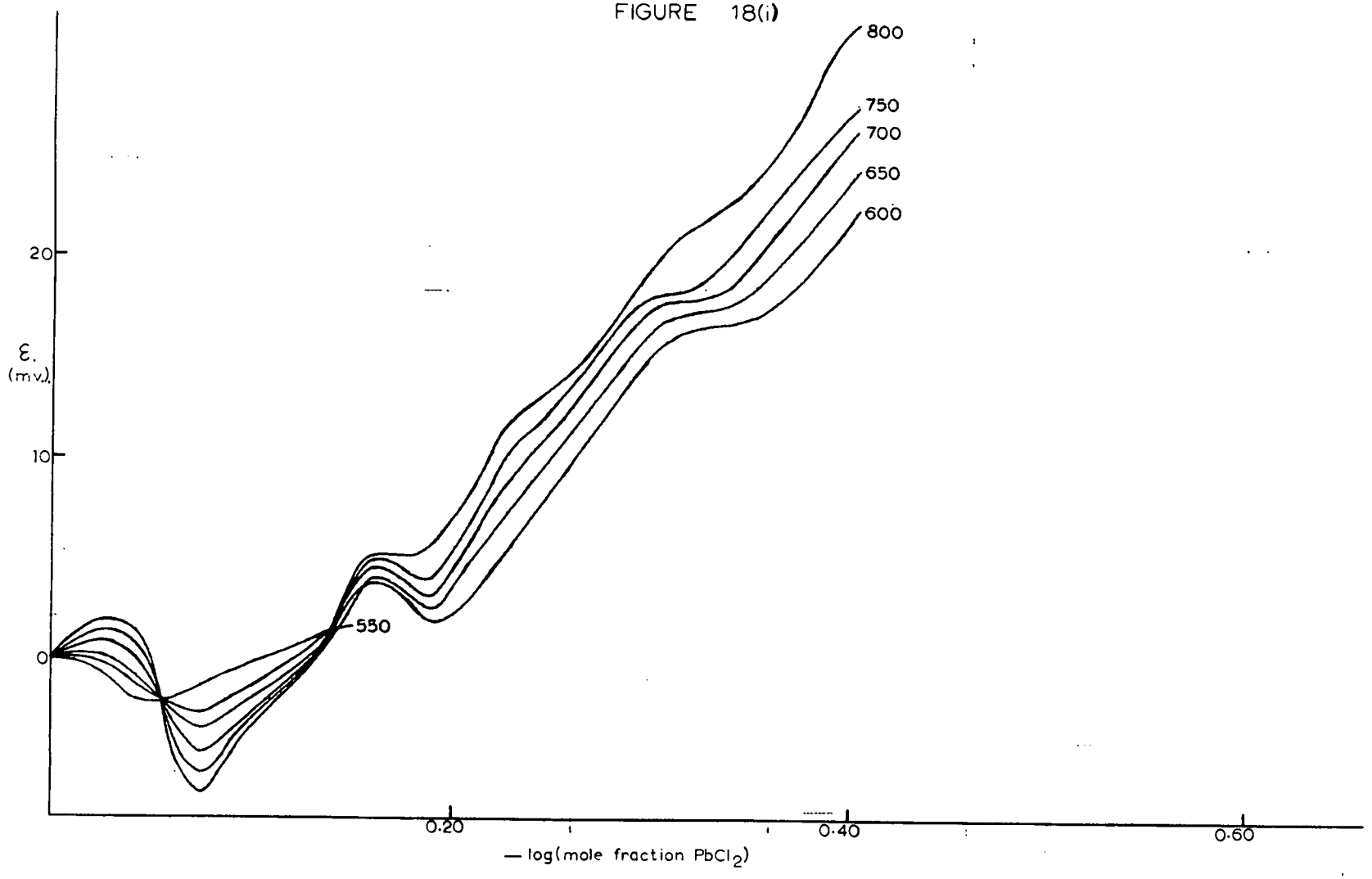
800
750
700
650
600
550
20
10
0
ε.
(mv.)
0.20
0.40
0.60
— log(mole fraction PbCl2)

FIGURE 18(ii)

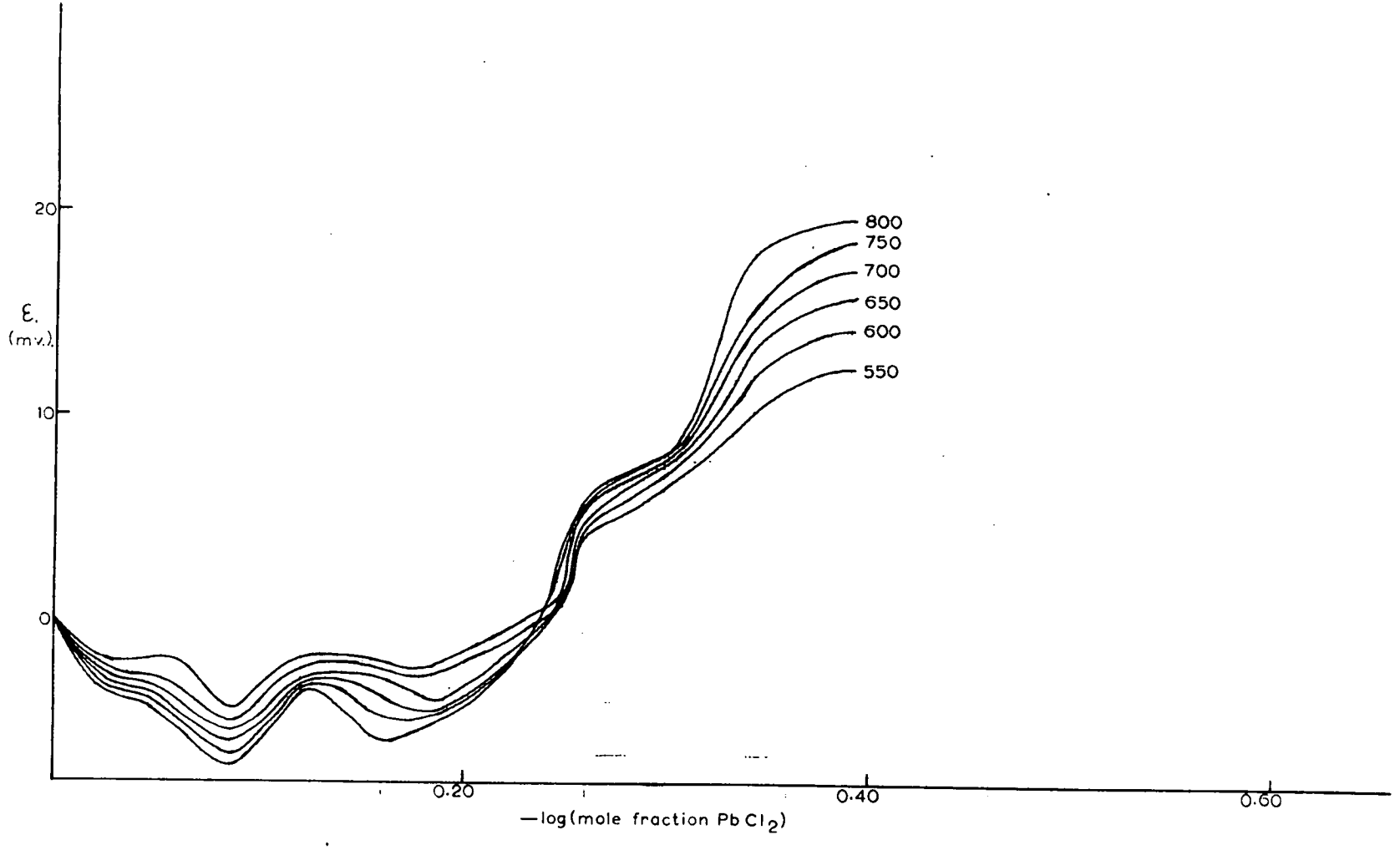
20
10
0
E.
(m.v.)
800
750
700
650
600
550
0.20
0.40
0.60
—log(mole fraction PbCl2)

FIGURE 19

Plot of diffusion potential against temperature for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr.

The numbers appended to the curves denote the composition of the mixture, appropriate to each curve.

FIGURE 19(1)

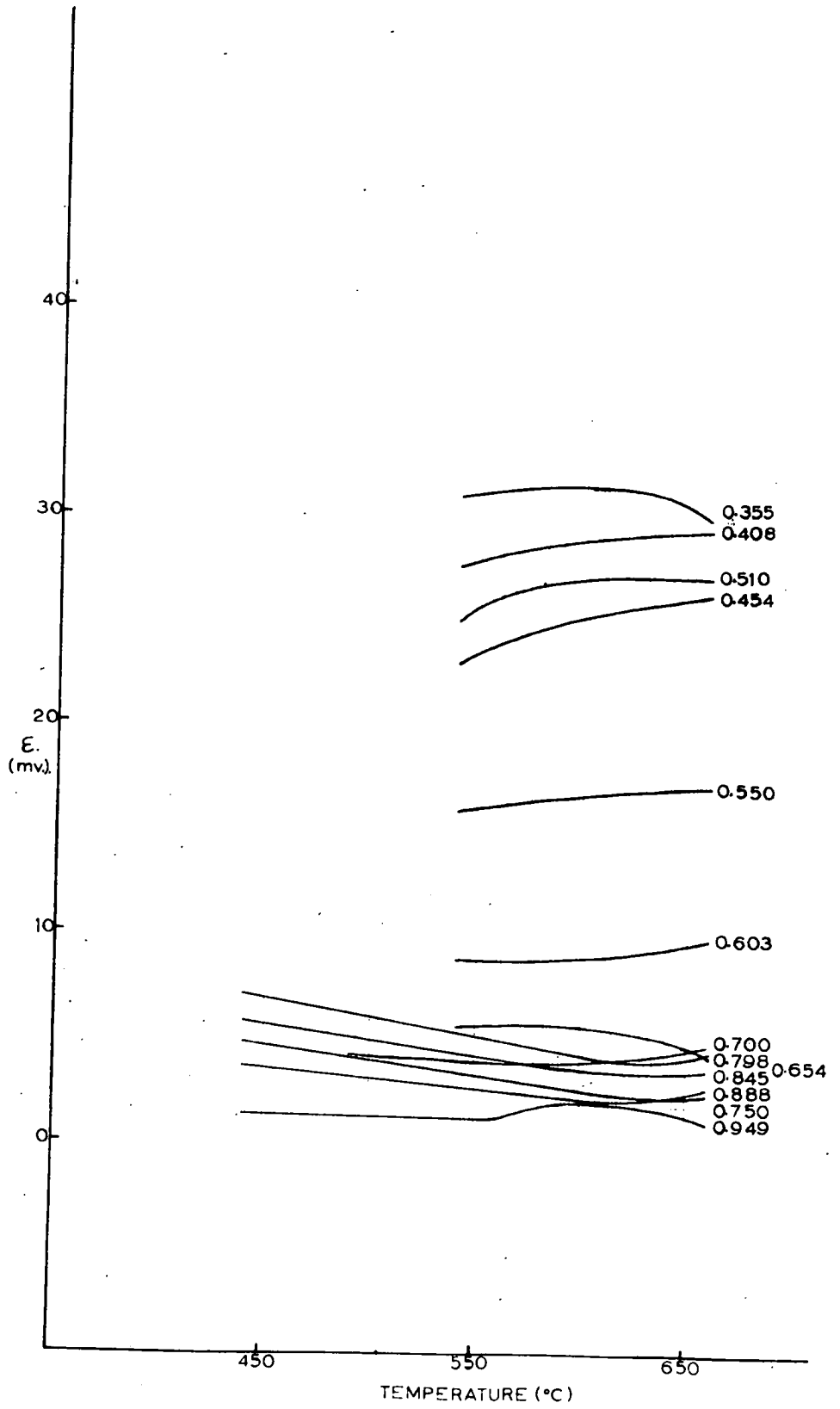
40
30
20
10
0
E.
(mv.)
0·355
0·408
0·510
0·454
0·550
0·603
0·700
0·798
0·654
0·845
0·888
0·750
0·949
450
550
650
TEMPERATURE (°C)

FIGURE 19(ii)

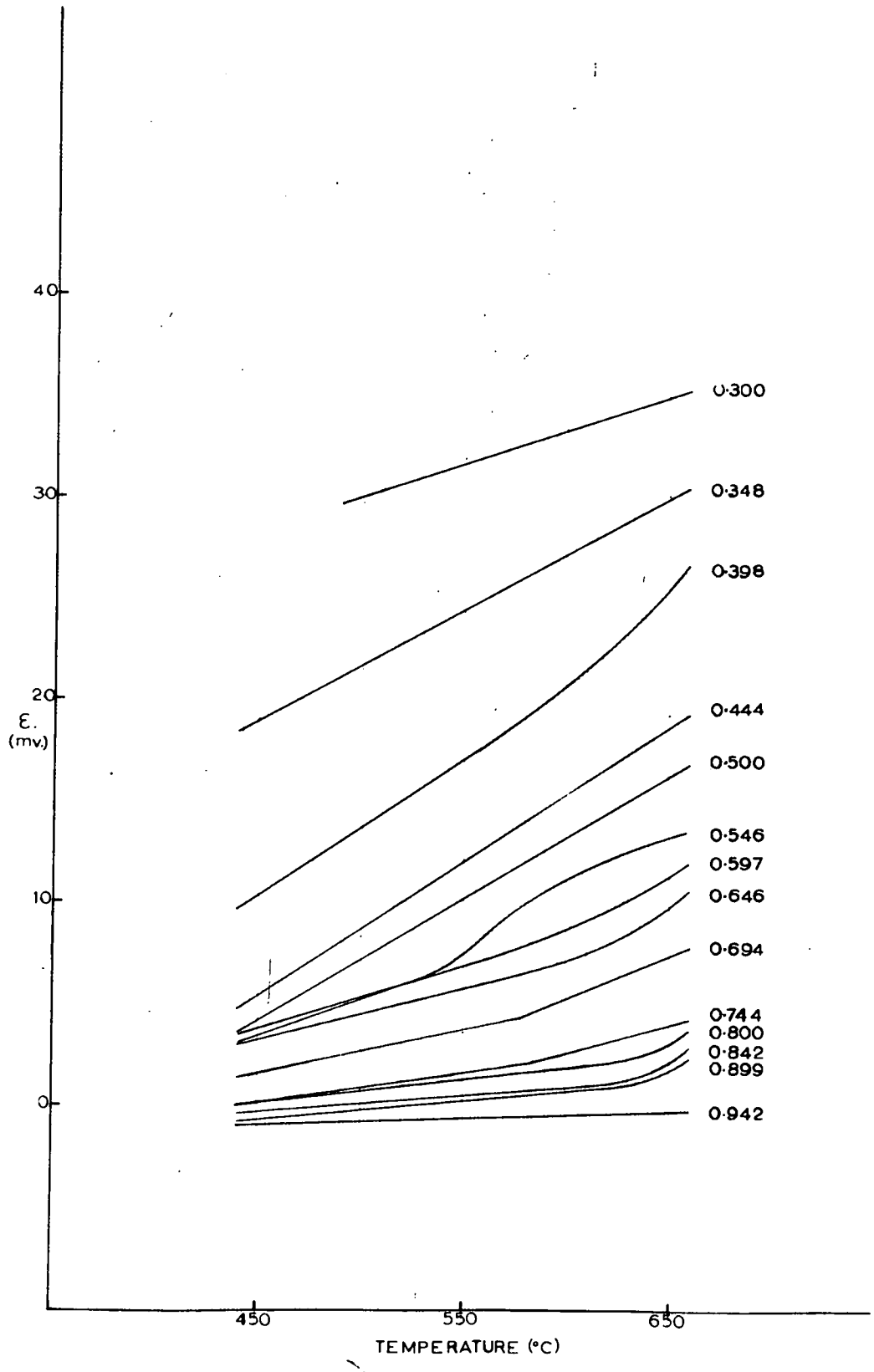
40
30
20
10
0
E.
(mv.)
0·300
0·348
0·398
0·444
0·500
0·546
0·597
0·646
0·694
0·744
0·800
0·842
0·899
0·942
450
550
650
TEMPERATURE (°C)

FIGURE 19(iii)

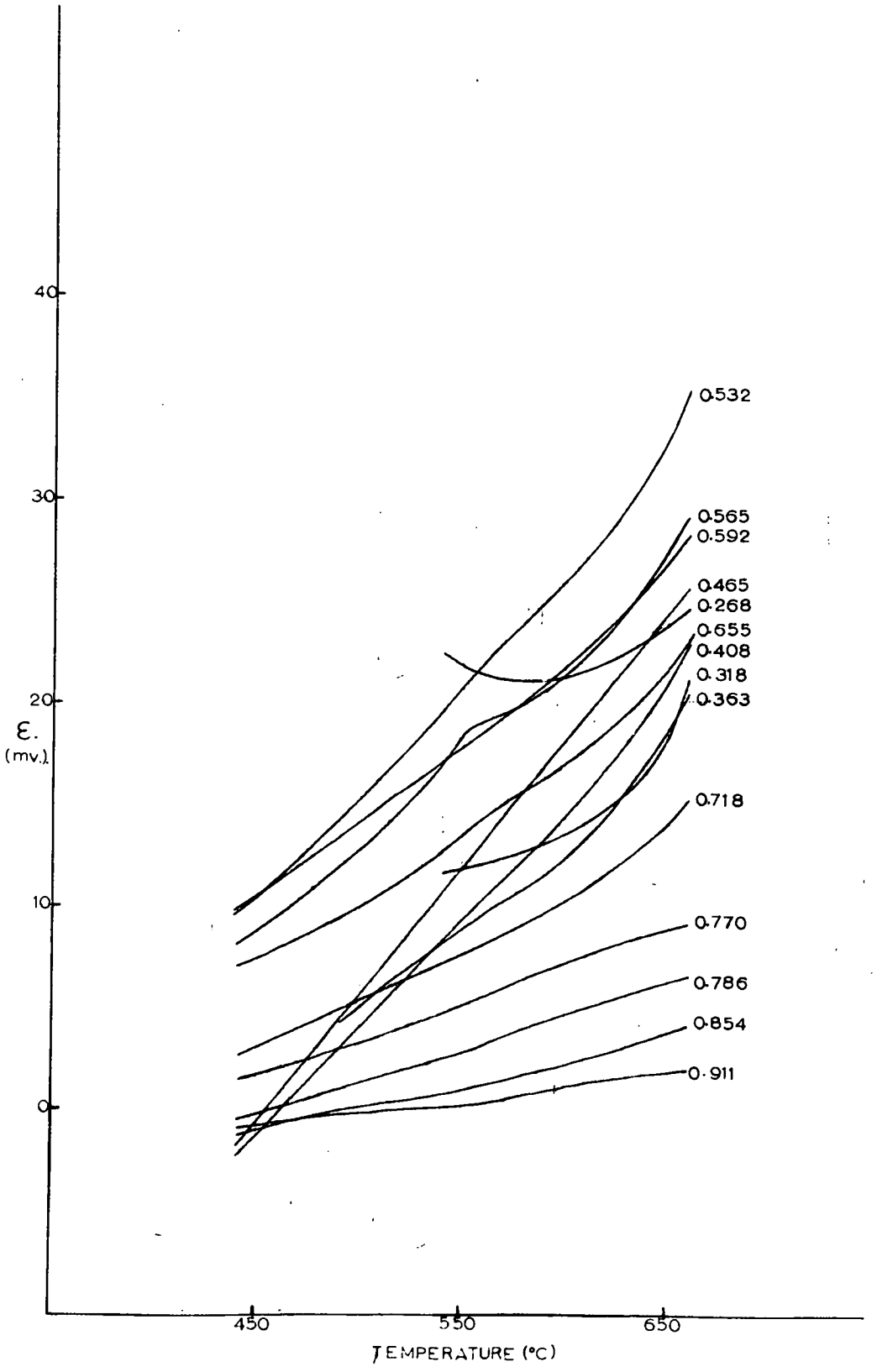

FIGURE 20

Plot of diffusion potential against temperature, for chloride systems.

(i) $PbCl_2$ - CsCl

(ii) $PbCl_2$ - RbCl

The numbers appended to the curves denote the composition of the mixture, appropriate to each curve.

FIGURE 20(i)

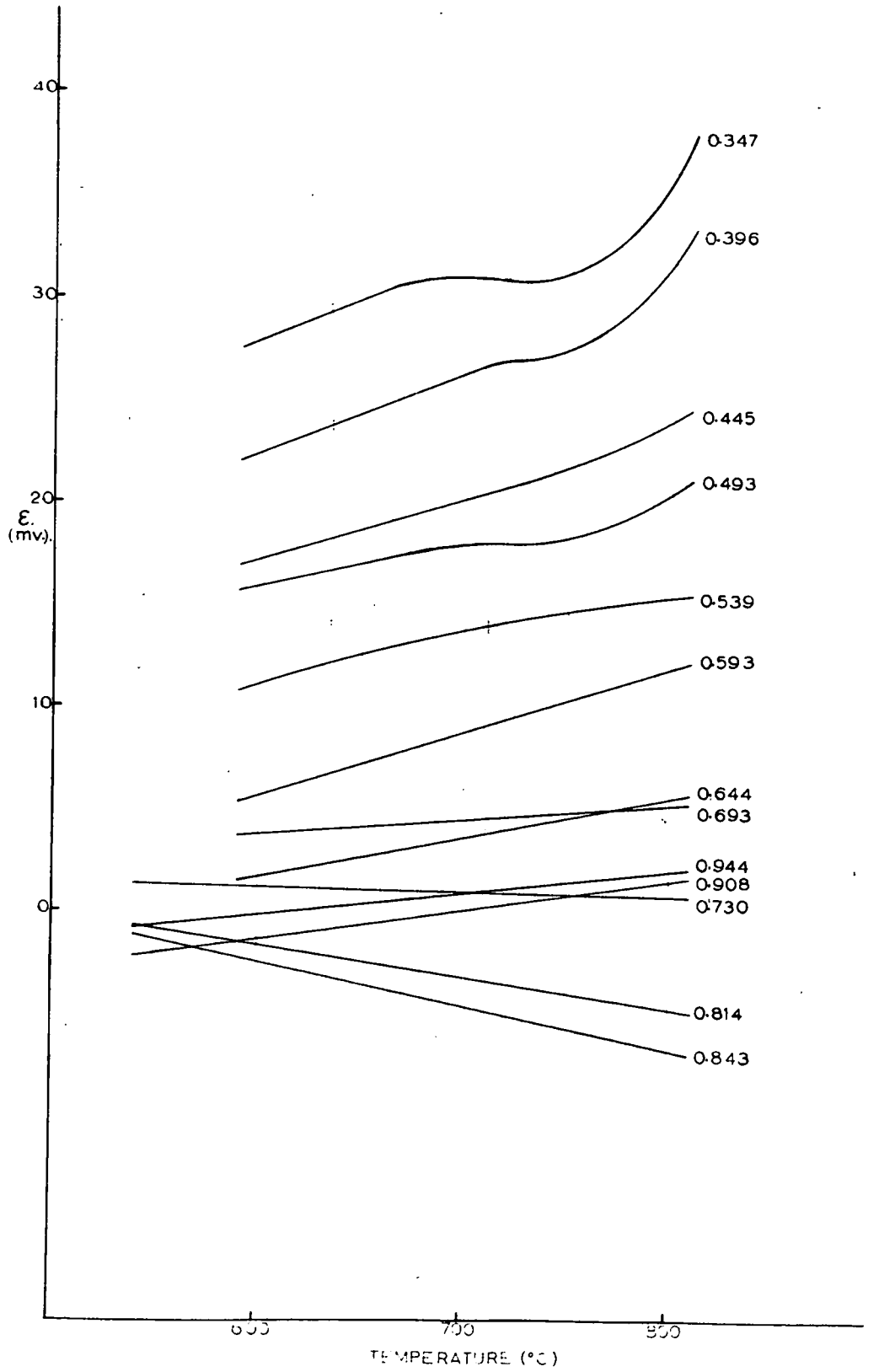
40
30
20
10
0
ε.
(mv).
0·347
0·396
0·445
0·493
0·539
0·593
0·644
0·693
0·944
0·908
0·730
0·814
0·843
600
700
800
TEMPERATURE (°C)

FIGURE 20(ii)

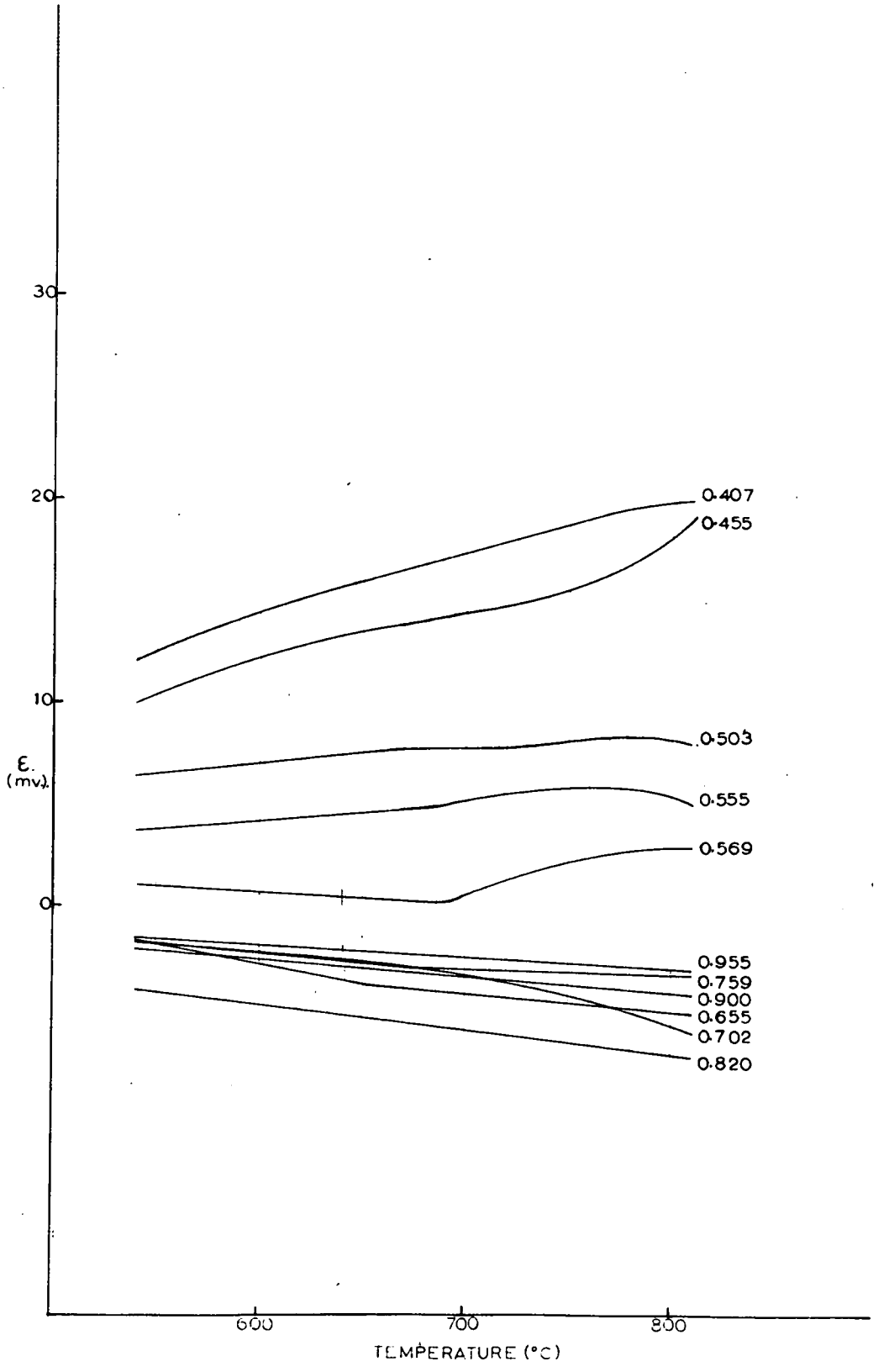
30
20
10
0
E. (mv).
0·407
0·455
0·503
0·555
0·569
0·955
0·759
0·900
0·655
0·702
0·820
600
700
800
TEMPERATURE (°C)

Table 7. : System $PbBr_2$ - RbBr

x_{PbBr_2}	$\mathcal{E}$ /T relationships	T'
0.942	= -2.51 + 0.0034T, (450-650).	-
0.744	= -6.67 + 0.0150T, (450 - 586.9);	
	= -14.3 + 0.0280T, (586.9 - 650).	586.9
0.694	= -7.90 + 0.0210T, (450 - 576.2);	
	= -20.0 + 0.0420T, (576.2 - 650).	576.2
0.500	= -22.77 + 0.0598T, (450 - 650).	-
0.444	= -25.55 + 0.0682T, (450 - 650)	-
0.348	= -5.80 + 0.0548T, (450 - 650)	-
0.300	= 12.90 + 0.0340T, (500 - 650).	-

Table 8. (i): System $PbCl_2$ - CsCl

x_{PbCl_2}	$\mathcal{E}$ /T relationships	T'
0.944	= -6.56 + 0.0106T, (550 - 800).	-
0.908	= -9.51 + 0.0136T, (550 - 800).	-
0.843	= 10.50 - 0.0217T, (550 - 800).	-
0.814	= 7.94 - 0.0161 T, (550 - 800).	-
0.730	= 2.59 - 0.0024T, (550 - 800).	-
0.693	= -0.42 + 0.0070T, (600 - 800).	-
0.644	= -9.86 + 0.0192T, (600 - 800).	-
0.593	= -13.08 + 0.0312T, (600 - 800).	-

Table 8. (ii) : System $PbCl_2$ - RbCl

x_{PbCl_2}	$\mathcal{E}$ /T relationships	T'
0.955	= 1.53 - 0.0058T, (550 - 800).	-
0.900	= 2.49 - 0.0084T, (550 - 800).	-
0.820	= 2.33 - 0.0120T, (550 - 800)	-
0.759	= 3.70 - 0.0100T, (550 - 668.0);	668.0
	= -0.98 - 0.0030T, (668.0 - 800).	

D . DISCUSSION

1. Accuracy of Experimental Data

(a) E.M.F's of concentration cells with transference.

The measurements of E.M.F. were made to within 0.001 mv. Under equilibrium conditions, i.e. temperature and E.M.F. invariant, there was no detectable fluctuation in E.M.F. Hence, the individual measurements of E.M.F. are presumed to be accurate to within ± 0.001 mv.

As discussed previously (see Experimental) the E.M.F. of such a cell as

$$\mathrm{Pb} \;\big|\; \underset{\text{pure}}{\mathrm{PbX_2}} \;\Big\|\; \underset{x_{\mathrm{PbX_2}} = 0.25}{\mathrm{PbX_2 + MX}} \;\big|\; \mathrm{Pb}\ ,$$

of E.M.F. E_1, was obtained not by direct measurement but by addition of the measured E.M.F's of a series of cells, such as

$$\mathrm{Pb} \;\big|\; \underset{\text{pure}}{\mathrm{PbX_2}} \;\Big\|\; \underset{x_{\mathrm{PbX_2}} = 0.75}{\mathrm{PbX_2 + MX}} \;\big|\; \mathrm{Pb}\ ,\ \text{E.M.F.}\ E_2\ ,$$

$$\mathrm{Pb} \;\big|\; \underset{x_{\mathrm{PbX_2}} = 0.75}{\mathrm{PbX_2 + MX}} \;\Big\|\; \underset{x_{\mathrm{PbX_2}} = 0.50}{\mathrm{PbX_2 + MX}} \;\big|\; \mathrm{Pb},\ \text{E.M.F.}\ E_3\ ,\ \text{and}$$

$$\mathrm{Pb} \;\big|\; \underset{x_{\mathrm{PbX_2}} = 0.50}{\mathrm{PbX_2 + MX}} \;\Big\|\; \underset{x_{\mathrm{PbX_2}} = 0.25}{\mathrm{PbX_2 + MX}} \;\big|\; \mathrm{Pb}\ ,\ \text{E.M.F.}\ E_4\ ;$$

$$E_1 = E_2 + E_3 + E_4.$$

If the uncertainty in E_i ($i = 2, 3, 4$) is ± 0.001 mv. then the uncertainty in E_1 is ± 0.003 mv. at most. Such composition changes as occurred would have introduced an uncertainty of magnitude not greater than ± 0.007 mv.,

and hence the measured E.M.F's are considered to be accurate within ± 0.01 mv.

This analysis of errors applies to the measurements made on all systems except $PbCl_2$ - RbCl. This system was the first studied in this work, and the experimental technique was not fully mastered at that time. For this reason, the possible error in the E.M.F's relating to this system is higher - of the order ± 0.02 mv.

In investigation of the chloride systems, at temperatures above approximately 800°C the cell E.M.F's tended to fluctuate markedly, and large deviations from the linear plots were observed. A similar effect was encountered by Richards[1] in his work on concentration cells. Richards ascribed the effects to "asymmetry potentials". There is a possibility that, since the levels of bulk electrolyte and reference electrolyte in the cell were different (approximately 3 mm. difference), diffusion through the disc (due to the greater hydrostatic head of pressure on the reference electrolyte) could have taken place, thereby setting up electrokinetic potentials. In principle, such potentials could introduce significant error into the measured values of cell E.M.F. Richards, using cells almost identical to those employed in the present work, carried out a thorough investigation of such effects. He measured the E.M.F's of cells of the type

$$Pb \;|\; PbCl_2\ (pure) \;\|\; PbCl_2\ (pure) \;|\; Pb$$

1. Bloom and Richards, to be published; Richards, Ph.D. Thesis, University of New Zealand (1956).

with three different porous discs, over a range of temperature. It was found that the asymmetry potentials had low values (ca. 0.01 mv.) at temperatures close to 500°C; in general the potentials increased in magnitude with increasing temperature. Richards states [1] : "...at 800°C, (the potential) would introduce errors greater than the experimental errors. The marked increase in this effect in the temperature range 750° - 820° ... serves as confirmation that chemical attack of the glass and other spurious effects sets in above the approximate temperature 760°, invalidating the recording of E.M.F. data. ...below the upper temperature limit, the asymmetry E.M.F's were not only small, but were constant and reproducible during a run." Richards used cells and discs made from a high softening point barium aluminosilicate glass, which is much less resistant to attack by molten salts than is the pure quartz which was utilised in the present work. Hence effects due to chemical attack of the containing vessels and discs would almost certainly be very much smaller in this work than in that of Richards. It was found in the present work that the same cell components could be used for at least 20 runs before etching of the silica was noticeable, provided the temperatures at which measurements were made were not too high. At higher temperatures, of the order 800°C, however, it was observed that attack of the silica was more pronounced, especially in the region of the surface of the electrolytes and almost always when a noticeable amounts of oxyhalides were present. Oxyhalides (particularly red lead oxybromides)

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1. Richards, Ph.D. Thesis, University of New Zealand (1956)

were always present (unavoidably) to a small extent on the surface of the melts, and chemical attack of the silica appeared to take place largely as a result of the presence of oxyhalides. When these were present in only very small amounts attack was negligible. Further, attack of the silica was noticeable only at high temperatures, even though oxyhalides were present in the melt at lower temperatures.

There was additional evidence to suggest that electrokinetic potentials were negligibly small. The transport number work (discussed in Chapter 2) indicated that in the cells used for those measurements electrokinetic effects were not appreciable. In the concentration cells, some of the evidence which suggested the virtual absence of electrokinetic effects were :

(i) the levels of reference electrolyte and bulk electrolyte did not change appreciably during a run and composition changes were in general very small, indicating only slight transference through the porous disc;

(ii) the appearance of fluctuations and corresponding uncertainty in E.M.F's was a discontinuous phenomenon, with respect to temperature. It was never apparent below approximately 800^{o}C with chloride mixtures and in no temperature range was this effect observed with bromide mixtures;

(iii) the cell E.M.F. was found to be independent of disc porosity, except for "superfine" discs.

It is considered, therefore, that within the range of temperatures at which cell E.M.F's were measured (i.e. less than ca. 800^{o}C) negligible error was introduced by electrokinetic effects. It is suggested

further, that the principal cause of the erratic behaviour of the cells at temperatures above about 800°C was attack of the silica due to oxyhalides present in the melt.

The upper limit to the temperatures at which the E.M.F's of bromide containing cells were measured was set by the tendency of the bromide mixtures to decompose markedly (evolving bromine) at temperatures higher than about 650 - 700°C, thereby changing the compositions of the electrolytes.

The thermocouple used for temperature measurement was found, by calibration, to be accurate to within 0.5°C at temperatures up to the freezing-point of silver (960.5°C). There were undoubtedly small errors in measurement and the temperature of the molten electrolyte may have varied radially within the cell, to a small extent. Since the molten salts have relatively high thermal conductivities, the temperature differential would have been very small. Overall, it is considered that the maximum possible error in temperature measurement was of the order ± 1°C.

Thus, the possible error in E.M.F. is, for low values of E.M.F., of the order 1 - 2%; the error decreases for higher values of E.M.F.

The mean deviation of points from the computed line of best fit describing the variation of E.M.F. with temperature was not greater than about 1%.

(b) E.M.F's of concentration cells without transference

The values of the E.M.F's of the appropriate cells

without transference were derived from the E.M.F's of experimental cells of the type

$$Pb \mid PbX_2 \mid X_2 \qquad \ldots I$$

$$Pb \mid PbX_2 + MX \mid X_2 \qquad \ldots II$$

The cell without transference could be set up by combining I and II back to back :

$$Pb \mid PbX_2 \mid X_2 \,,\, X_2 \mid PbX_2 + MX \mid Pb \qquad \ldots III$$

Cell III is equivalent to the concentration cell without transference

$$Pb \mid PbX_2 \;\|\; PbX_2 + MX \mid Pb \qquad \ldots IV$$

If the E.M.F. of cell I is E^o and that of cell II is E^1, then the E.M.F of the cell without transference is given by

$$E = E^1 - E^o \,.$$

From the known values of E^o and E^1 the values of E were thus derived. The values of E^o and E^1 were quoted (in the sources of the data) to 0.1mv. Assuming that these E.M.F's are accurate to within 0.2 mv., the possible error in E is $\pm$ 0.4 mv. Allowing for small error s in plotting and in interpolation of the E.M.F. / composition isotherms, the maximum error in E is probably about $\pm$ 0.5mv.

(c) Diffusion Potential

The greatest source of error in the values of diffusion potential lies in the values of the E.M.F's of the concentration cells without transference; the errors in the E.M.F's of the cells with transference are negligible in comparison.

Hence it is considered that the values of diffusion

potential are probably accurate to within ± 0.5 mv. This is a very large error, in comparison to the magnitude of the observed diffusion potentials (of the order 0 - 36 mv.), particularly for the small values of diffusion potential. It is to be regretted that measurements of E.M.F. of cells such as I and II have not been made with substantially higher precision, and that the E.M.F's of cells such as III have not been measured directly. Until much more accurate measurements are made, the values of diffusion potential, derived from them, will inevitably have large errors associated with them, of the order ± 1.5 to ± 30%, depending on the magnitude of the diffusion potential.

Although the absolute magnitudes of the diffusion potentials are quite uncertain (for low values of the diffusion potential), it is striking that the shapes of the diffusion potential / composition isotherms (Figures 15 and 16) are remarkably similar for all six systems investigated in this work. Furthermore, the variation of diffusion potential with temperature (Figures 19 and 20) is in almost all cases very regular. In fact, in those cases for which linear dependence on temperature was found, the mean deviations from linearity were very small. These observations suggest that the actual errors in the values of diffusion potential may be considerably smaller than has been estimated.

(d) Analysis

All volumetric equipment used in analysis was calibrated, "A" grade Standard. Using the methods of analysis outlined previously (see Experimental) all titrations were reproducible to within 0.01 ml. The maximum

possible error in the titrations, therefore, was probably not larger than $\pm$ 0.005 ml. which represents, in a titre of 10 ml. an uncertainty of $\pm$ 0.05%. Errors in weighing out samples etc. are considered to have been negligible. Since two titrations per analysis were required (one being standardisation of the sodium molybdate solution, the possible error in the analysis was about 0.1% (i.e. $\pm$ 0.001 in mole fraction).

2. General Discussion of Experimental Data

(i) Preliminary

Before proceeding to discuss in detail the experimental data obtained, it is necessary to outline the purpose and aims of the discussion, and the method of approach which is to be used.

We wish, in the first place, to disclose, by comparison of the data for all systems investigated, those properties of the molten salt mixtures which are characteristic of systems of the general type PbX_2 - MX (where X and M have the same connotation as before). Having done so, our aim is to set up a series of basic postulates relating such characteristic properties to the structure of the molten salt electrolytes, basing subsequent deductions on these basic postulates.

Further, the nature of the systems studied is such that it should be possible to elucidate the relative effects, if any, of regularly varying radius of both alkali metal cation and halide ion on the behaviour of the

concentration cells.

We shall suppose, in treating of the concentration cells with transference, that the "dissection" of the cell E.M.F. into three terms, i.e. two electrode potential terms and a liquid junction potential (diffusion potential) term, is not only a valid procedure but in fact the only valid procedure. This being the case, it should be possible to group the properties and behaviour of the cells into two classes - those which are related to the electrode reactions on the one hand, and those which are due, on the other hand, to the transport of ions across the liquid junction.

It is to be noted that Guggenheim [1] does not regard this dissection of the cell E.M.F. as a rigorous procedure. In treating the cell

$$\text{Cu} \mid \text{Zn} \mid \begin{matrix}\text{Solution I} \\ \text{containing } Zn^{2+}\end{matrix} \mid \begin{matrix}\text{Solution II} \\ \text{containing } Ag^{+}\end{matrix} \mid \text{Ag} \mid \text{Cu}$$

Guggenheim assumes the presence of one anion (NO_3^-) in both solutions I and II, and derives the formula

$$FE_t = \left[\frac{1}{2}\mu^{Zn}_{Zn} - \frac{1}{2}\mu^{I}_{Zn(NO_3)_2} + RT \ln M^{II}_{NO_3^-}\right]$$

$$+\left[\mu^{I}_{NO_3^-} - \mu^{II}_{NO_3^-} + RT \ln M^{II}_{NO_3^-}\right]$$

$$-\left[\mu^{Ag}_{Ag} - \mu^{II}_{AgNO_3} + RT \ln M^{II}_{NO_3^-}\right]$$

for the E.M.F. of the cell. He states : "We now have a formula for E (E_t) containing three terms in $[\ ]$ of which the first relates only to the Zn electrode and the solution around this electrode and the last relates

1. Guggenheim, "Thermodynamics" North-Holland, Amsterdam (1957)

only to the Ag electrode and the solution around this electrode. The middle term on the other hand is independent of the nature of the electrodes and relates to an anion present in both solutions. One might be inclined to call the first of these three terms the electrode potential of the Zn electrode, the second the liquid - liquid junction potential and the last the electrode potential of the silver. Such a procedure is harmless provided that it is realised that

(a) this decomposition (i.e. dissection) of E into three terms is affected by our arbitrary choice of the anion NO_3^- for use in our formulae;

(b) other alternative decompositions of E into three terms can be obtained by the arbitrary choice of some other ion instead of NO_3^- in our formulae;

(c) any such decomposition is no more or less fundamental than another;

(d) there is in general no means of decomposing E into three terms which is less arbitrary than the one described."

Notwithstanding Guggenheim's comments, many workers appear to regard the procedure as the correct one (e.g. Kirkwood and Oppenheim[1]). We shall in this work employ this particular dissection procedure as a basic postulate in descriptions of the cells.

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1. Kirkwood and Oppenheim, "Chemical Thermodynamics", McGraw - Hill, New York. (1961).

(ii) The Variation of Concentration Cell E.M.F. with Temperature

To the author's knowledge, no other E.M.F. measurements have been made to date, for concentration cells with transference containing as electrolytes the six molten salt systems studied herein. Thus there is no basis for comparison of the present data with previously determined data.

The most striking feature of the temperature dependence of the E.M.F's measured in this work is the appearance of changes in slope of the E.M.F. / temperature plots. This feature appears to have been observed only once previously, by Grube and Rau [1] in their investigations of the cells

$$Pb \mid 2PbCl_2 + KCl \,\|\, PbCl_2 \mid Pb \text{ , and}$$

$$Pb \mid PbCl_2 + KCl \,\|\, PbCl_2 \mid Pb.$$

If the data of Grube and Rau for these two cells are plotted against temperature, the (linear) plots exhibit changes in slope at temperatures in the vicinity of 600°, 570 - 580° and 550°C. Unfortunately the data of Grube and Rau is imprecise, hence it is not possible to draw conclusions from it with confidence. In contrast to the results of Grube and Rau, Richards data [2] for the E.M.F's of concentration cells containing mixtures of $PbCl_2$ with $CdCl_2$, NaCl and KCl were presented in such a way as to indicate that the E.M.F. / temperature relationship should be a single straight line for a given mixture. It is important to note however,

1. Grube and Rau, Z.Elektrochem., 40, 352 (1934)
2. Bloom and Richards, to be published; Richards, Ph.D.Thesis, University of New Zealand (1956)

that Richards measured E.M.F's at much wider temperature intervals than did the present author. The deviation of Richards" data from a single straight line is such that it is very likely that if there were more points on the plots, then a better representation of the data would have been a series of intersecting straight lines. It is the author's contention that the reason for the non-appearance of changes of slope in Richards' data is the small number of points on the plots. In other words, it is only because E.M.F's were measured at very small temperature intervals that the changes of slope appeared on the E.M.F / temperature plots in this work. For many mixtures the changes in slope are small - that they are significant is corroborated by the fact that the relative changes in slope are much greater than the mean deviation of the experimental points about the lines of best fit. Many of the slope changes are so small that if the number of experimental points had been very much less, then a single straight line representation would have been justifiable.

It is a basic postulate of this thesis that the changes in slope are real and that they have fundamental significance in respect of the constitution of the salt mixtures. It is further proposed, that the temperatures at which changes of slope occur are "characteristic" in that they are parameters which reflect characteristic changes in structure of the molten salts. The changes in structure are thought to be due to equilibria between complex ionic species in the melts.

It is instructive to group the observed temperatures

at which changes of slope in the E_t/T curves appear, around possible "characteristic temperatures". In the following such classification (Table 9) the "characteristic temperatures" (Tc^1) both for the bromide and for the chloride systems are included together. $\triangle$ denotes, for each group, the mean deviation from the mean value of Tc^1 and $\overline{Tc}^1$ is the mean value of Tc^1.

Table 9. Characteristic Temperatures, Tc' (°C).

782.2	768.5	745.2	726.5	697.0	672.3	659.9	643.9	626.9
787.1	763.1	743.5	721.6	696.3	681.2	663.3	636.2	628.0
776.7	755.2	736.0	716.4		677.6		635.3	627.0
778.8	754.0	735.2	716.9		685.8		643.8	629.1
782.4		739.1	713.2				642.5	631.5
776.8			708.0				650.2	625.2
785.0			711.6				646.1	631.2
773.1			728.3				638.2	624.1
778.2			709.1				634.6	632.1
778.8								627.7
								628.1
								626.6
$\overline{Tc'}$ 779.9	760.2	739.8	716.8	696.7	679.2	661.6	641.2	628.1
$\triangle$ ± 3.4	± 5.6	± 3.6	± 5.8	± 0.4	± 4.3	± 1.7	± 4.6	± 2.1
% 0.44	0.74	0.49	0.81	0.05	0.63	0.26	0.72	0.33

Table 9. (continued)

613.8	602.7	578.1	556.2	532.8	520.7	495.7	486.2	470.0	451.4	(428.4)
616.2	593.7	583.7	548.5	528.7	521.0	502.8	482.9	467.7	452.1	
619.3	590.2	579.0	547.0	534.6	517.4	494.7		466.9	444.4	
612.9	596.8	583.8	563.8	530.6	515.5	499.2		467.3		
616.3	605.3	580.4	564.5	528.2	518.0	498.2				
616.1	595.0	584.8	556.5	526.6	523.8	496.3				
614.8	605.5	583.2	551.2	527.3	509.5					
614.3	590.4	574.3	552.6	537.8						
616.5	601.6	573.5	558.7							
614.4	599.7	586.6	545.4							
615.7	607.5		546.0							
612.6	608.5		544.7							
619.1	597.8		545.5							
	597.0									
	604.0									
	602.0									
$\bar{f}c'$ 615.5	599.9	580.7	552.4	530.8	518.0	497.8	484.6	468.0	449.3	-
△ ± 1.5	± 4.8	± 3.7	± 5.9	± 3.2	± 3.9	± 2.3	± 1.7	± 1.0	± 3.3	-
% 0.24	0.80	0.64	1.07	0.60	0.75	0.46	0.35	0.21	0.74	-

At low temperatures the lead halide alkali halide mixtures are regarded here as containing large associations of ions, held together by predominantly ionic bonds, and with overall structure only slightly different from the structure of pure molten lead chloride. At higher temperatures these aggregates break up increasingly to form smaller, more tightly bonded species and at still higher temperatures the latter co-ordinate with further halide ligand to form increasingly isolated, covalently bonded lead-halide complexes. If the same type of change continued to occur at temperatures approaching the boiling point, it would be expected that the vapours of the salt mixtures would contain very large amounts of alkali halides, so that the partial pressures of alkali halide in the vapours would be much greater than the vapour pressure of pure alkali halide at the same temperature. Moreover, the relative increase in partial pressure of alkali halide, expressed as

$$(p - p^{o}) / p^{o}$$

should increase with increasing temperature : p^{o} is the vapour pressure of the pure salt at a given temperature and p is the partial pressure of alkali halide in the mixed vapour, at the same temperature. Let us denote the quantity $(p - p^{o}) / p^{o}$ by f. f is a function of the fugacity of the alkali halide; specifically

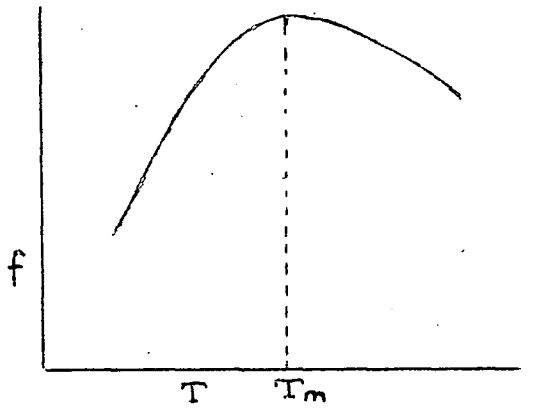
$$f = (\text{fugacity} - 1)$$

since

$$\text{fugacity} = (p / p^{o}).$$

f should show an overall increase with temperature, but this increase will not be monotonic. It is predicted that the plot of f against temperature will have at least one maximum, corresponding to the temperature at which the most strongly covalently bonded species is present in the molten salt, since this species will have the greatest tendency to escape into the vapour. For the salt systems discussed here, the ion PbX_3^- is probably the most strongly bonded of the species postulated although this species is not associated with the highest degree of covalent character of the salt as a whole.

The f / T curve should have a maximum value in the temperature range 680 - 700°C, due to the presence of the ion PbX_3^- in the salt, at this temperature. The curve should therefore have the approximate form:

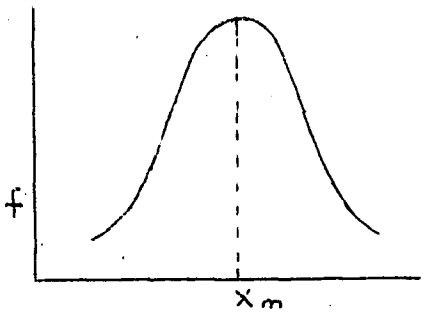


Tm is the temperature at which f is maximum and should have the value

$$Tm \qquad 690 \pm 10^{\circ}C.$$

Unfortunately there is (to the author's knowledge) no experimental data available with which this prediction may be tested.

From the assumption that PbX_3^- is the most strongly bonded species in the molten salt mixtures it follows that isotherms of the parameter f plotted against composition should show a maximum at the composition corresponding to 50 mole % PbX_2 - 50 mole % MX. Thus we predict a dependence of f on composition, of the form:



x_m is the composition (mole fraction of PbX_2) at which f has its maximum value, and

$$x_m = 0.5$$

The structural changes proposed above should be accompanied by changes in the energy of system. The changes should therefore be capable of detection by precise thermal analysis of the liquid mixtures. Unfortunately no such experiments have been conducted to date.

(iii) The Variation of Concentration Cell E.M.F. with Composition of the Electrolyte.

The E.M.F. / (mole fraction alkali halide) curves (Figures 11 and 12) for the various lead halide / alkali halide systems studied have several features in common. Particularly striking (and characteristic) are the points of inflexion on the curves. For the four bromide systems there is such a point in the region of 50 mole % alkali bromide, in each case. This point of inflexion is prominent in all the isotherms except those pertaining to the system $PbBr_2$ - KBr, in which it is rather indistinct. The isotherms for the systems $PbBr_2$ - RbBr and $PbBr_2$ - KBr show further points of inflexion at compositions corresponding to approximately 10 and 20 mole % alkali bromide, while for the system $PbBr_2$ - NaBr the corresponding points appear at compositions corresponding to 10 and 30 mole % NaBr. The isotherms for the $PbCl_2$ - CsCl system show less marked changes at about 5, 15 and 25 mole % CsCl, whereas the curves for the system $PbCl_2$ - RbCl show only one point o f inflexion, at approximately 65 mole % RbCl. It must be recognised, in relation to the isotherms for the latter system, that the data are not as

accurate for this system as are those for the other systems.

A more revealing representation of the dependence of cell E.M.F. on electrolyte composition is provided by the E.M.F. / -log x_{PbX_2} plots (Figures 13 and 14). In all cases except that of the 650°C plot for the system $PbBr_2$ - NaBr, the isotherms exhibit marked changes in slope at compositions which vary regularly with temperature (see Results, Tables 3 and 4.)

It is proposed that the linear regions of these isotherms delimit those composition regions in which particular (structural) types of complex ions exist. In the composition range marked by any one linear portion of the E.M.F. / -log x_{PbX_2} plots, therefore, the complex ions present in the melt have a common basic structure; in another composition range, the complex species have a different basic structure, and so on. We shall presume that the structures become increasingly covalently bonded with increasing proportion of alkali halide.

The variation of x_c (the composition at which a change of slope appears) with temperature is, in general, regular. The temperature dependence of the highest values of x_c for each system cannot be regarded as significant, because (a) the errors in the E.M.F. values are highest in those regions of composition corresponding to mixtures most rich in PbX_2 and (b), the lines which pass through the origin of coordinates, for each system (except the 650°C line for the system $PbBr_2$ - NaBr) are not calculated lines of best fit. Apart from these highest values of x_c however, the values increase with increasing temperature, in general. On

the basis of the interpretation proposed in the preceding section, increase of x_c with temperature is to be expected. Since the more covalently bonded species - which correspond to species containing a relatively high proportion of halide ligand - should be favoured at higher temperatures, therefore the compositions at which changes in structural type occur should correspond to mole fractions of lead halide which increase with increasing temperature.

The plots of the E.M.F's of the appropriate cells without transference against $-\log x_{PbX_2}$ are shown in Figures 21, (i) to (iv) and Figures 22, (i) and (ii) below. The lines are not calculated lines of best fit. These plots show definite changes of slope and are formally very similar to the corresponding plots of the E.M.F's of the cells with transference against $-\log x_{PbX_2}$.

Since the E.M.F. of the cell without transference is determined wholly by the electrode reactions taking place in the cell, there are apparently compositions at which the relationship between cell E.M.F. and composition, changes. These changes must be due to changes in the microscopic "structure" of the electrolyte, of such a nature as to change the thermodynamic activity of PbX_2 in the mixture, since E is theoretically a single linear function of $\log a_{PbX_2}$. The structure changes are due then, to changes in the degree of interaction between lead and halogen species in the melt, and it is just such changes which we have deduced from the plots of E.M.F. of cell with transference against $-\log x_{PbX_2}$.

The plots of the E.M.F's of the cells without transference allow the contributions to the E.M.F's of the cells with transference, from

FIGURE 21

Plot of E.M.F. of concentration cells without transference against the negative logarithm of the mole fraction of lead halide, for bromide systems.

(i) $PbBr_2$ - CsBr

(ii) $PbBr_2$ - RbBr

(iii) $PbBr_2$ - KBr

(iv) $PbBr_2$ - NaBr

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 21(i)

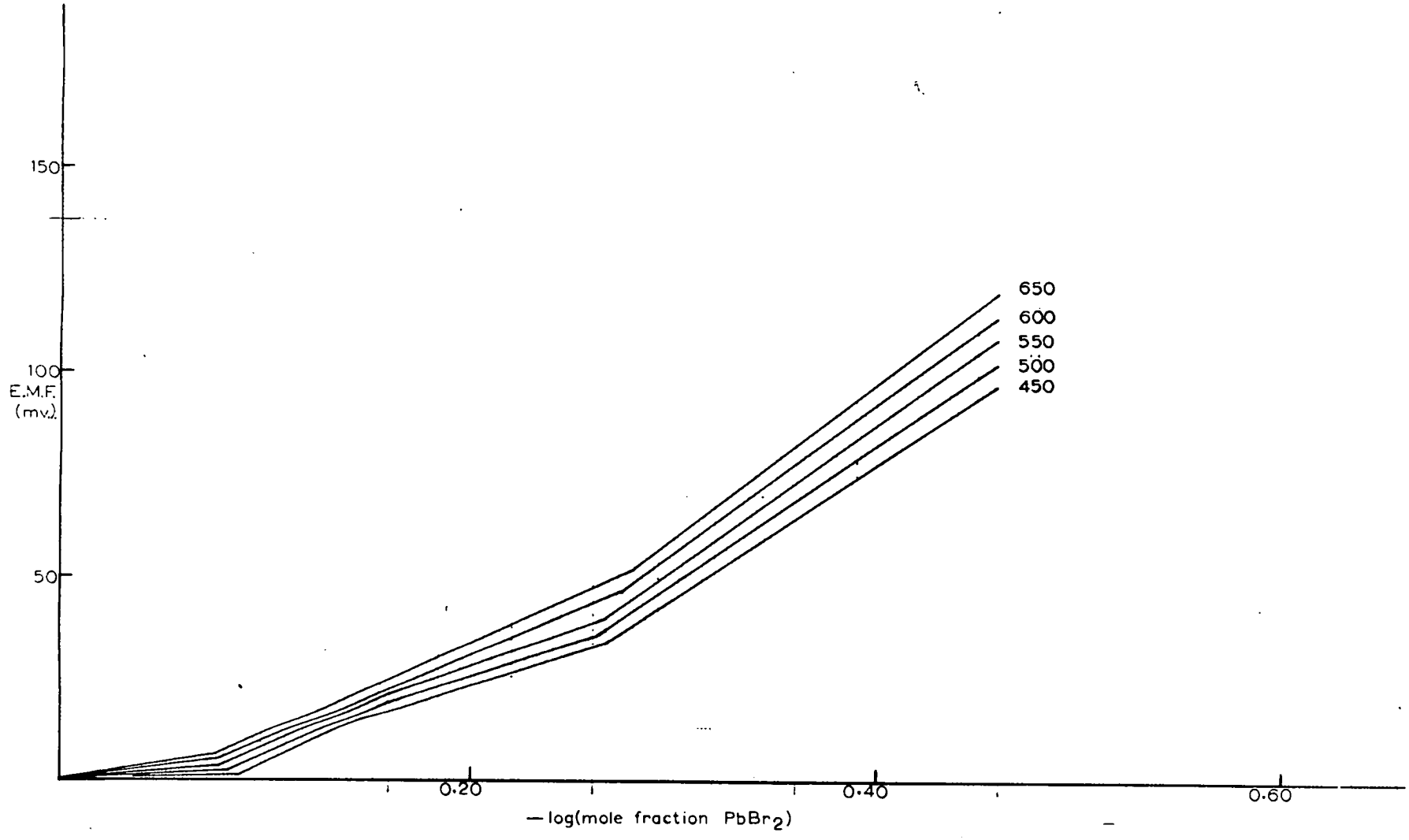

150
100
E.M.F.
(mv.)
50
650
600
550
500
450
0.20
0.40
0.60
— log(mole fraction $PbBr_2$)

FIGURE 21(ii)

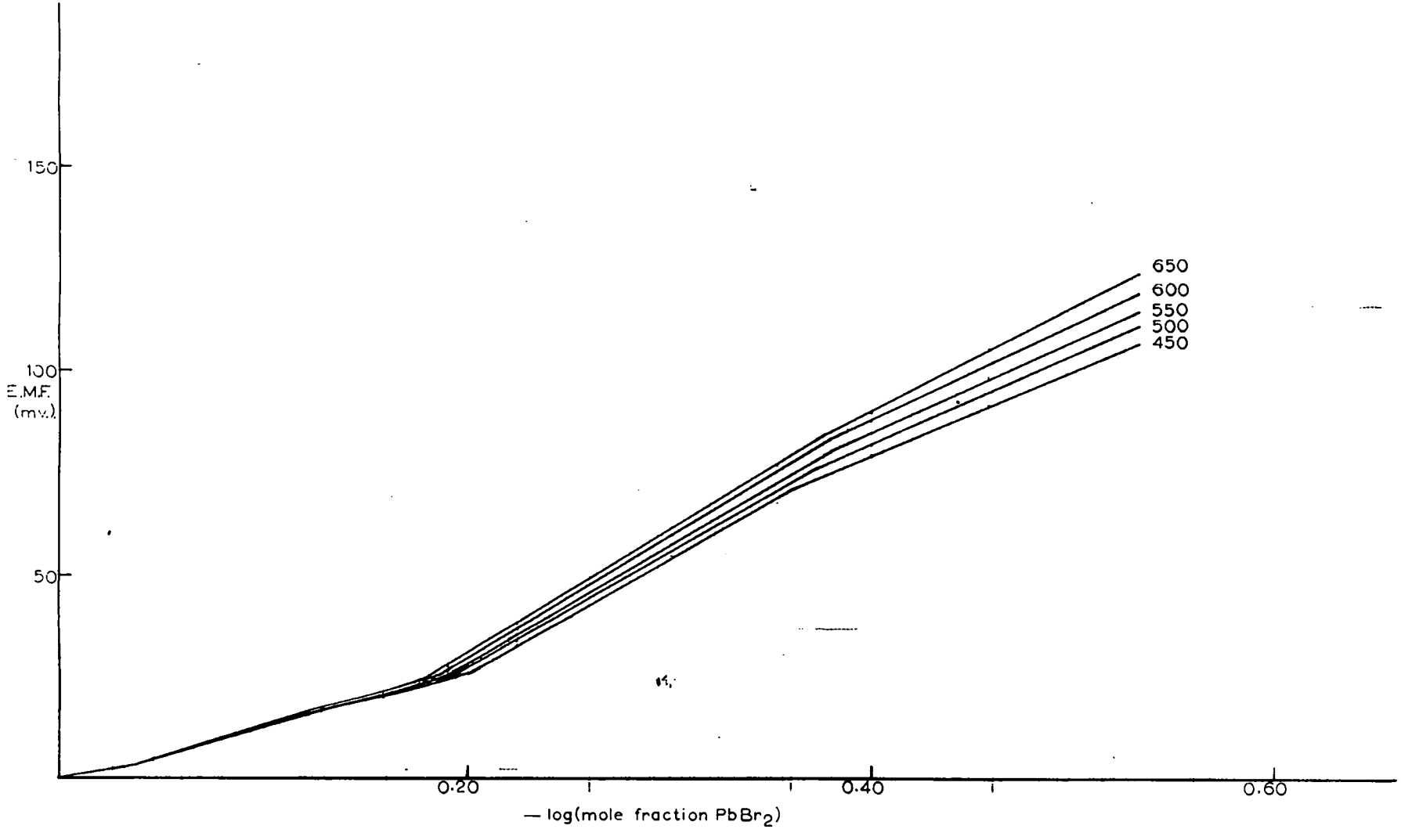

150
100
50
E.M.F.
(mv.)
650
600
550
500
450
0.20
0.40
0.60
— log(mole fraction $PbBr_2$)

FIGURE. 21(iii)

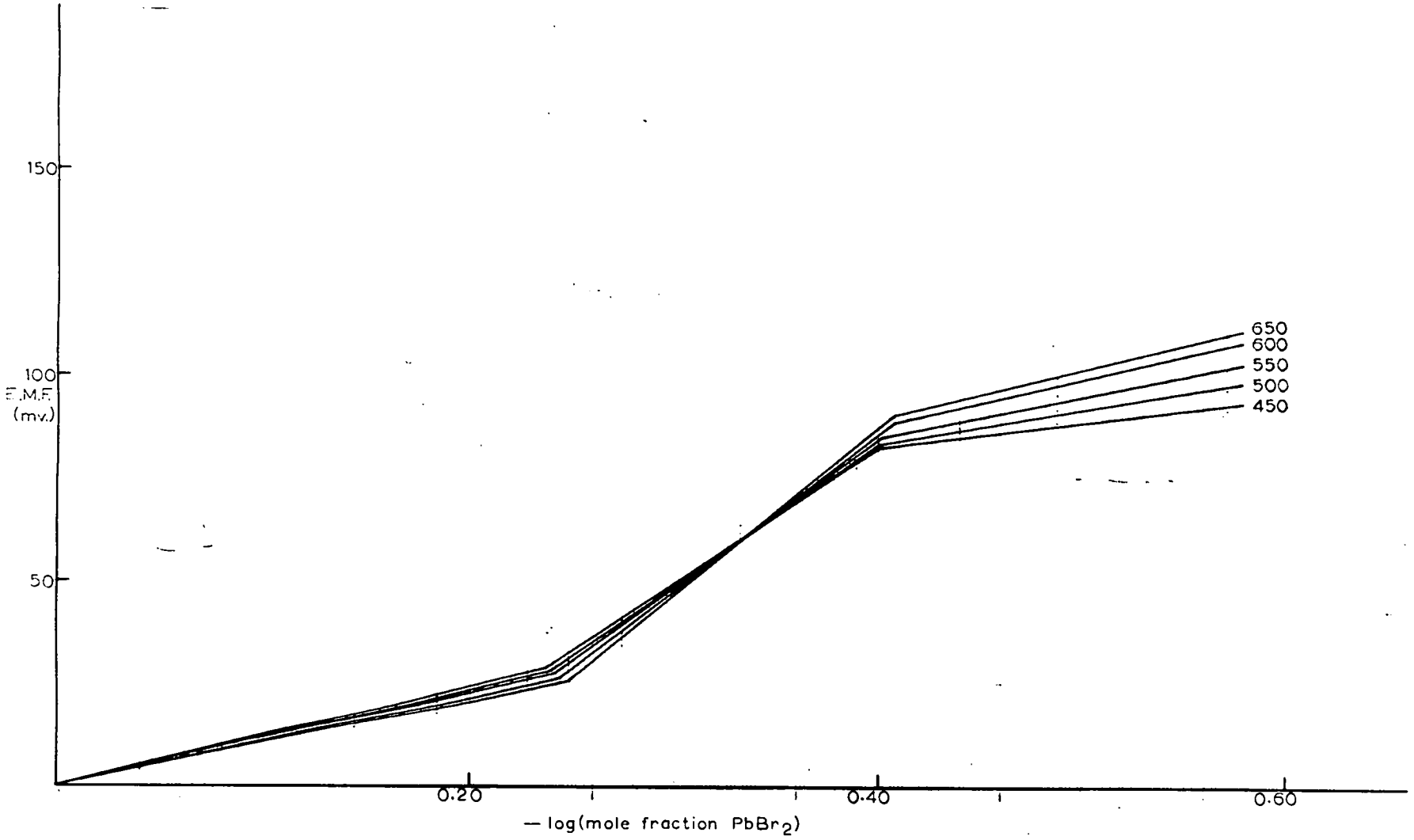


FIGURE 21(iv)

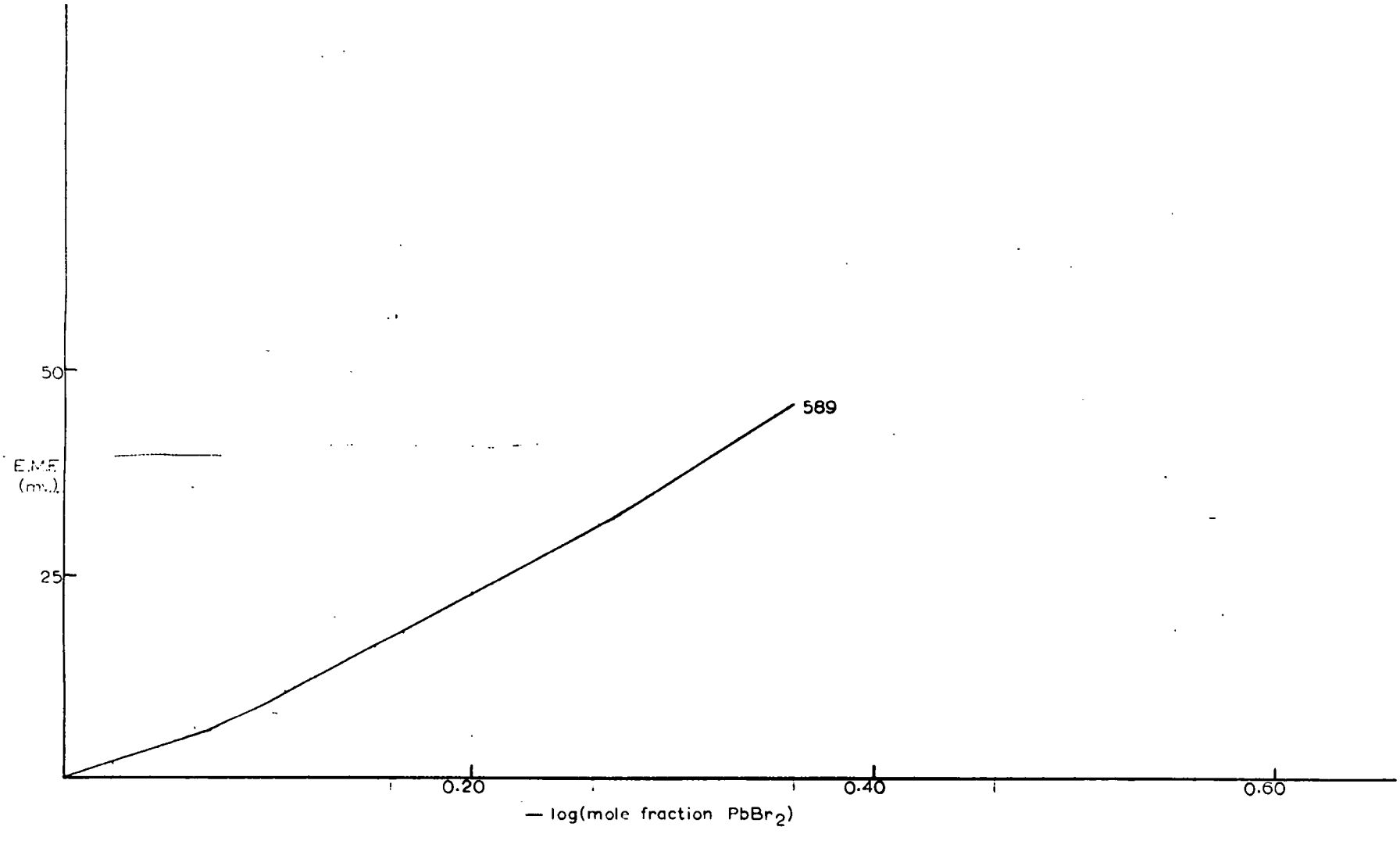


FIGURE 22

Plot of E.M.F. of concentration cells without transference against the negative logarithm of the mole fraction of lead halide, for chloride systems.

(i) $PbCl_2$ - CsCl

(ii) $PbCl_2$ - RbCl

The numbers appended to the curves denote the temperature appropriate to each isotherm.

FIGURE 22(i)

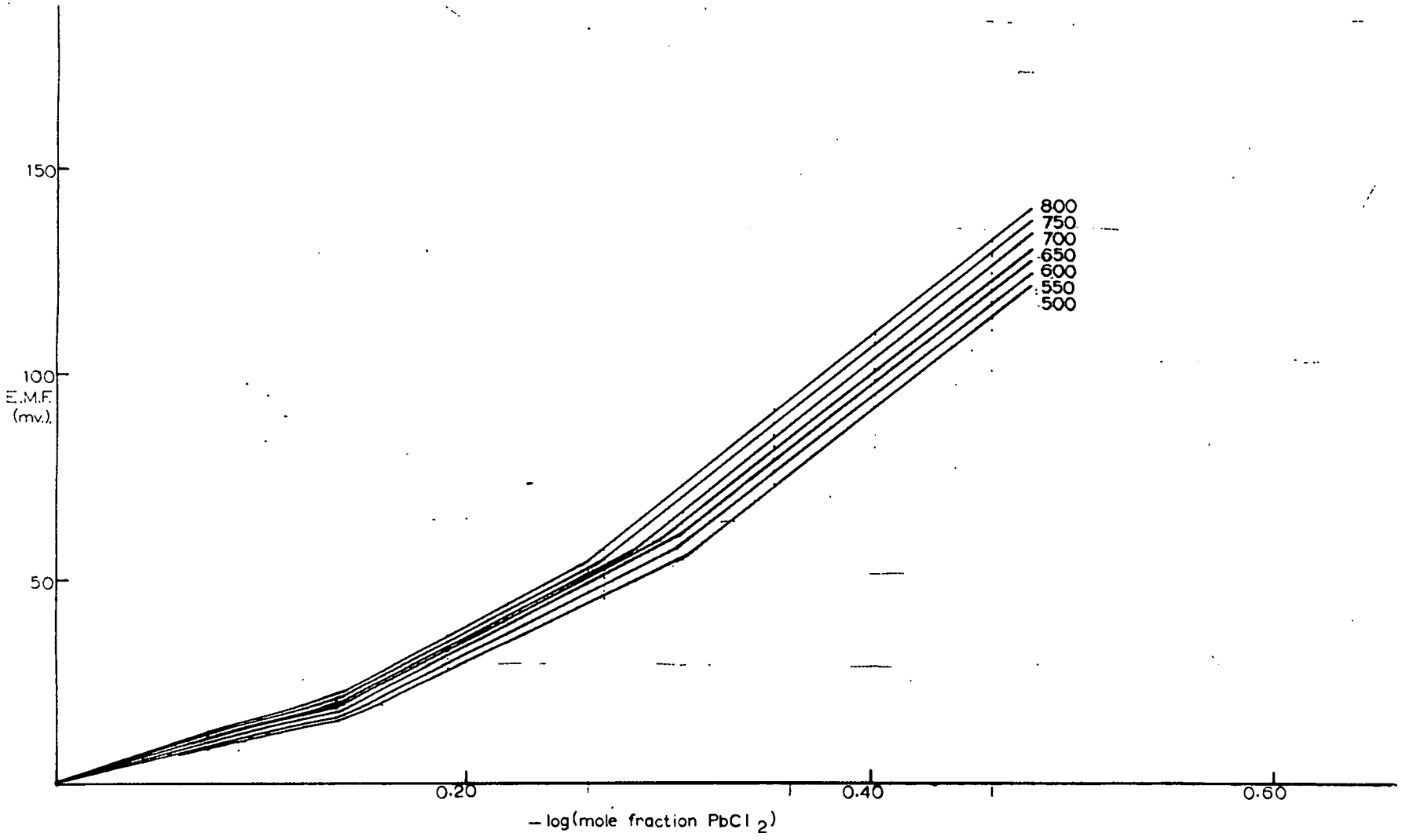
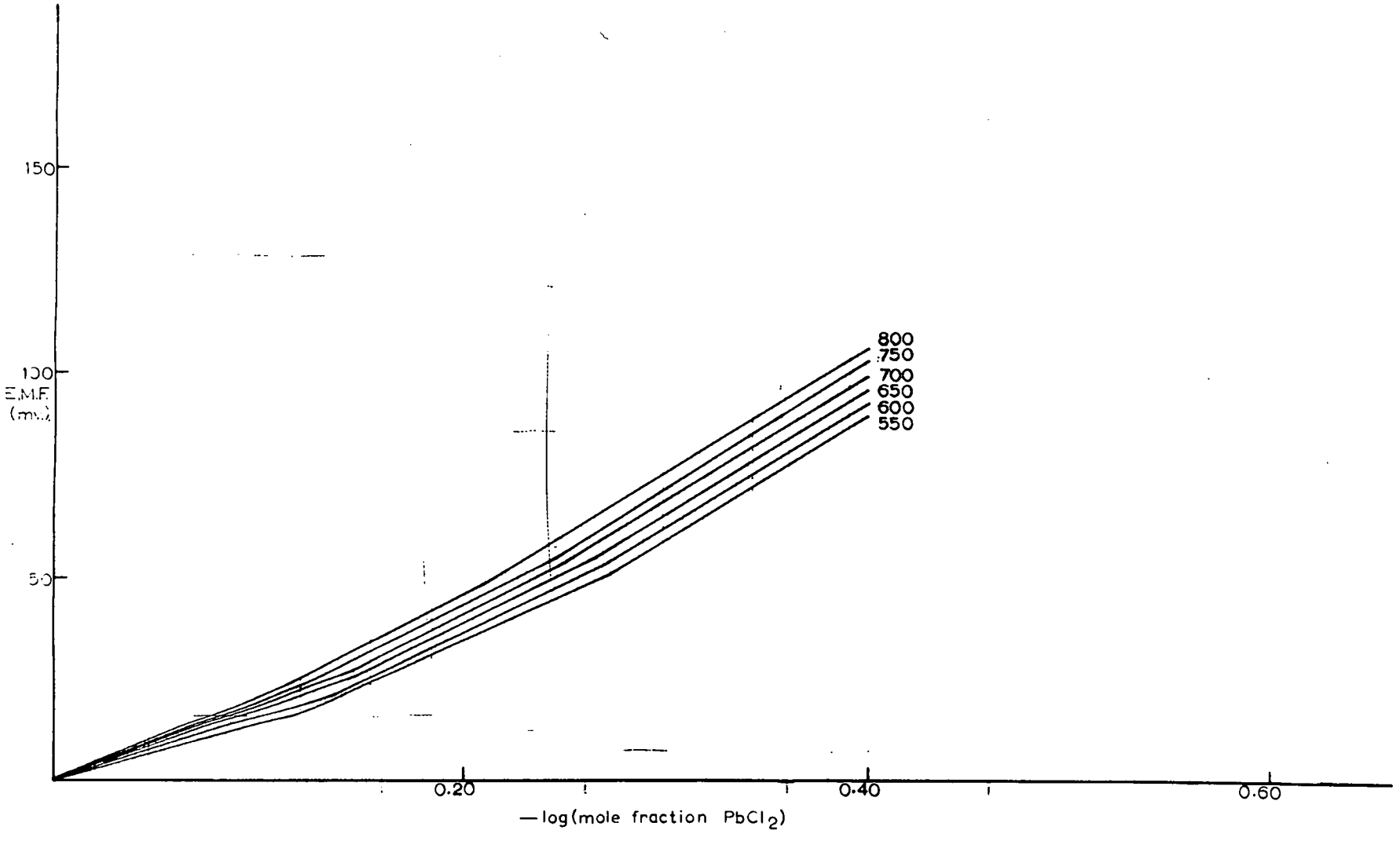

150
100
50
E.M.F. (mv.)
800
750
700
650
600
550
500
0.20
0.40
0.60
– log(mole fraction PbCl 2)

FIGURE 22(ii)


150
100
E.M.F.
(mv.)
50
800
750
700
650
600
550
0.20
0.40
0.60
— log(mole fraction $PbCl_2$)

the electrode reactions and from the processes taking place at the liquid junction to be separated.

Deductions concerning the structure of molten salt mixtures have been made previously by various workers, on the basis of studies of concentration cells with transference. Grube and Rau[1] analysed the data from their measurements of the E.M.F's of cells containing $PbCl_2$ - KCl mixtures and concluded that the addition of potassium chloride to lead chloride not only produces simple dilution of the lead chloride but is also accompanied by an intimate interaction of the two salts, leading to complex ion formation. This deduction was later confirmed by Zhurin[2] from measurements of the E.M.F's of cells containing the same electrolytes. Concentration cells containing molten salt electrolytes were used by Pletenev and Rosov [3] in order to examine the chemical combinations between the salt of a metal under study and the salts used as the media. They noted that the E.M.F. of concentration cells varies in linear fashion with the negative logarithm of the mole fraction of the salt of the metal being studied and that the nature of this linear dependence is different for cases in which chemical compounds are present in, or absent from, the melt. For salts which do not form any compounds (indicated by thermal analysis), the experimental points were found to lie on a single straight line passing through the origin of the coordinates. The slopes of these

1. Grube and Rau, Z.Elektrochem., 40, 352 (1934)
2. Zhurin, Trudy Leningr. ind. inst., 1, issue 1, 74 (1939)
3. Pletenev and Rosov, Zh.Fiz.Khim., 9, 854 (1937)

straight lines were found to be close to the theoretical value of the prelogarithmic coefficient (2.303 RT / ZF). Behaviour of a different kind was observed in those salt mixtures for which thermal analysis indicated the formation of chemical compounds. In such cases, the points were observed to lie on two straight lines (to a first approximation) and Pletenev and Rosov deduced that the point of intersection of the two lines corresponds to that dilution of the salt at which the salt being studied is completely bound up in a complex ion. The data of Pletenev and Rosov for the salts cadmium chloride and lead chloride, each dissolved in KCl - LiCl eutectic, show a change in slope (denoted by x_c in the present work) at a composition (mole fraction of KCl) greater than that corresponding to the mole ratios 4 KCl : 1 $PbCl_2$ and 4 KCl : 1 $CdCl_2$. This was interpreted as indicating a "certain excess" of KCl with respect to the complexes $\left[PbCl_6^{4-}\right]\left[4K^+\right]$ and $\left[CdCl_6^{4-}\right]\left[4K^+\right]$. It was further noted that at dilutions higher than that at which the salt exists only in the form of a complex, the E.M.F. varied in accordance with ideality, i.e. the slope of the upper straight line was close to the theoretical value.

It is difficult to compare the results of the present work with those of Pletenev and Rosov, because these workers investigated primarily mixtures very rich in alkali halide (KCl), in contrast to the mixtures more rich in lead halide which have been studied by the present author. However, the conclusions reached by Pletenev and Rosov are in qualitative agreement with the conclusions drawn by the present author, from the concentration cell studies.

(iv) The Variation of Diffusion Potential with Temperature

In general, the diffusion potential / temperature plots are linear at relatively low temperatures - i.e. at temperatures approaching the melting point of the lead halide in question - particularly for mixtures rich in lead halide.

Generally, the shape of the plots changes regularly with composition, particularly in the system $PbCl_2$ - CsCl. It is proposed that variation in the form of these curves with composition is a sensitive indication of changes from one type of structure to another, due to a changing relative proportion of alkali halide to lead halide.

The plots show quite clearly the effects on the structure of two basic factors determining the structure, namely (a) the relative concentrations of alkali halide and lead halide and, (b) the temperature of the molten electrolyte. Some of the curves, for particular compositions, show a change in form at certain temperatures; these changes in shape are presumably caused by structural changes due to the influence of the temperature.

In accordance with our postulate concerning the dissection of the cell E.M.F. into the three separable terms, it follows that deductions concerning the structures of the salts, derived from considerations of the diffusional potential (e.g. from the variations of ε with T and x_{PbX_2}), are in principle relevant only to those processes taking place at the junction and not necessarily to the electrode reactions.

(v) The Variation of Diffusion Potential with Composition of the Bulk Electrolyte

The dependence of $\mathcal{E}$ on x_{PbX_2} is illustrated by Figures 15 and16. There are several features of the curves which are common to all six systems investigated. One common feature is the fully or partially resolved maxima; it is postulated that these maxima and the compositions at which they occur are intimately related to structural changes which take place within the molten salt electrolytes under consideration. In every case there is a maximum (or "latent" maximum) at the composition corresponding to the 1 : 1 mole ratio of lead halide to alkali halide. It is proposed that this maximum value of $\mathcal{E}$ is to be correlated with the presence in the mixtures of the ion PbX_3^-, More rigorously, we shall postulate that the maximum in $\mathcal{E}$ at the 1 : 1 composition is due to the presence, in the salts, of a structural arrangement of halide ligands about central lead "atoms" represented stoichiometrically by the formula PbX_3^-.

The other maxima which appear on the $\mathcal{E}$ / x_{PbX_2} curves do not occur at the same compositions for each system and will not be discussed in detail in this section, since we are concerned here with the general features of the curves common to all the systems considered.

The plots of $\mathcal{E}$ against -log x_{PbX_2} are very similar in form to the $\mathcal{E}$ /x_{PbX_2} plots, indicating that the diffusion potential is not a linear function of -log x_{PbX_2}. The functional relationship is apparently a very complicated one in fact.

We shall defer more detailed discussion of the diffusion potential until a later section, in which the relationship between the structure

of the electrolyte and the magnitude and sign of the diffusion potential will be examined.

3. The Formation, Stability and Structure of Complex Ions in Molten Lead Halide - Alkali Halide Mixtures

It is proposed that there should be three major factors governing the formation and stability of complex ions in these mixtures:

(i) the temperature of the system,

(ii) the concentration of free ligand relative to that of the central metal, i.e. the relative propertions of alkali halide and lead halide,

(iii) the polarising power of the alkali metal cation.

Accordingly we shall make use of three basic postulates:

Postulate I - The degree of covalent character of the liquid salt mixtures increases with increasing temperature;

Postulate II - The degree of covalent character of the liquid salt mixtures increases with increasing relative proportion of ligand to central metal;

Postulate III - The degree of covalent character of the liquid salt mixtures varies inversely with the polarising power of the alkali metal cation.

We shall examine these three postulates, the evidence for their validity and their ramifications, in more detail.

(a) Postulate I.

This postulate has already been discussed to some extent, in the general discussion of the dependence of cell E.M.F. on temperature. The validity of the postulate cannot be either substantiated or negated at present, by available experimental data. However, there are experimental observations which suggest that it is a good approximation.

For example, it is known that several salts exist in the gaseous state in the form of molecules, a specific example being lead chloride, whose vapour contains [1], almost exclusively, $PbCl_2$ molecules. It has been found also that the vapours of the alkali metal chlorides contain few ions and that they are constituted mainly by polymeric molecular species such as dimers, trimers etc. [2] It follows therefore that at temperatures approaching the boiling points of such salts the formation of covalently bonded "molecules" must take place to a large extent. The formation of the molecules may be a discontinuous phenomenon, i.e. it is possible that no molecules are formed until a certain temperature is reached. It seems more likely however, that it is a gradual process which begins at temperatures well below the boiling point, implying that the degree of covalent character of the melt should increase with increasing temperature. These experimental observations are in accord with Postulate I.

(b) Postulate II

According to Postulate II the degree of covalent character increases with increasing proportion of ligand. This implies that if the total degree of covalent character of the melt as a whole could be measured then this quantity should increase with increasing mole fraction of alkali halide. As pointed out previously the strength of individual Pb - X bonds (assuming that the strength of the bond is directly proportional to the degree of covalent character possessed by the bond) will not increase

1. Barton, Ph.D. Thesis, University of New Zealand (1956); Welch, M.Sc. Thesis, University of New Zealand (1958)
2. Miller and Kusch, J.Chem.Phys., 25, 860 (1950)

continuously with x_{MX}. It will in fact reach a maximum at that composition at which the species PbX_3^- predominates, because in this species the bond strength is almost certainly greater than in species such as PbX_4^{2-}, PbX_5^{3-}, PbX_6^{4-} etc.

(c) Postulate III

As a first approximation we shall take the polarising power of an alkali metal cation (ϕ_i) to be directly proportional to the surface charge density of the ion. Thus

$$\phi_i \propto (Z_i / 4 \pi r_i^2)$$

where Z_i is the charge on the ion i and r_i is its radius. For the series of alkali metal cations, Z_i is constant (unity) and hence we may rewrite ϕ_i as

$$\phi_i = k (1 / r_i^2)$$

where k is a proportionality constant. Using the values for the ionic radii $r_{Na^+} = 0.98$ Å, $r_{K^+} = 1.33$ Å, $r_{Rb^+} = 1.48$ Å and $r_{Cs^+} = 1.69$ Å, we obtain for ϕ_i (in the appropriate units)

$$\phi_{Na^+} = 1.02k, \phi_{K^+} = 0.57k, \phi_{Rb^+} = 0.46k, \phi_{Cs^+} = 0.35k.$$

Rationalising ϕ_{Cs^+} to unity, we obtain

$$\phi_{Na^+} = 2.9k', \phi_{K^+} = 1.63k', \phi_{Rb^+} = 1.31k', \phi_{Cs^+} = 1.00k'.$$

The units of ϕ_i are not important in the present context because the relative values only are relevant to the present discussion.

As alkali metal halide MX is added to pure PbX_2, the effects of temperature and increasing proportion of ligand X^- should be invariant, to a first approximation, for all alkali halides MX. Thus we may consider the effect of the varying polarising power of the alkali metal

cation, independently of the other two effects. According to the relative polarising powers of the M^+ ions (above) Na^+ should have approximately three times the inhibiting effect on covalent bond formation as does Cs^+, and K^+ and Rb^+ a much smaller effect, but still appreciably larger than that of Cs^+.

It follows hence that the first change in slope in the E.M.F. / -log x_{PbX_2} plots should occur at progressively lower values of x_c (if postulate III is obeyed) through the series of systems from PbX_2 - CsX to PbX_2 - NaX, and this (highest) value of x_c (denoted by $x_{c'}$) should be approximately inversely proportional to ϕ_1.

In fact this is not the case; the E.M.F. / -log x_{PbX_2} curves indicate rather that $x_{c'}$ has a common value (approximately) for the systems $PbBr_2$ - CsBr and $PbBr_2$ - RbBr, and a second value common to the two systems $PbBr_2$ - KBr and $PbBr_2$ - NaBr. It appears therefore that either the effects of temperature and proportion of ligand are not independent of the effect of ϕ_1 (i.e. approximation above not justified) or else there is a critical value of ϕ_1, say ψ_c, such that for $\phi_1 > \psi_c$, $x_{c'}$ has a value largely independent of the nature of the alkali halide, while for $\phi_1 < \psi_c$, $x_{c'}$ has a different (greater) value, again independent of the nature of the alkali halide.

The second-highest values of x_c (denoted by $x_{c''}$) are very similar for the four systems $PbBr_2$ - CsBr, $PbBr_2$ - RbBr, $PbBr_2$ - NaBr and $PbBr_2$ - RbCl. For the systems $PbBr_2$ - KBr and $PbCl_2$ - CsCl the values of $x_{c''}$ are substantially lower. In this range of composition

it appears therefore, that for the first four systems above, the polarising power of the cation M^+ has little effect on the nature of the structural entities present in the melt. Presumably the relative proportion of ligand has the predominant influence in this composition range. An examination of the E.M.F. / -log x_{PbX_2} plots shows that for the system $PbBr_2$ - CsBr the slope increases at x_c", for $PbBr_2$ - RbBr the slope increases by a lesser amount and for $PbBr_2$ - NaBr, the slope decreases at x_c". It is feasible therefore that for the $PbBr_2$ - KBr system the change in slope at the composition corresponding to x_c" for the other systems would be quite small, and its non-appearance may well be due to uncertainties in the experimental data of about the same magnitude as the change in slope. It is possible, therefore, that the value of x_c for the system $PbBr_2$ - KBr which was denoted by x_c" should actually be denoted x_c"'.

For the system PBr_2 - NaBr alone, there is a third value of x_c (x_c"') which is close to the value of x_c" for the system $PbCl_2$ - CsCl. The appearance of this third value of x_c , for the system $PbBr_2$ - NaBr, is proposed to be due to the high polarising power of the ion Na^+ . The magnitude of ϕ_{Na^+} is probably sufficiently great to distort two basically similar structures to such an extent that the two distorted structures achieve configurations sufficiently different to lead to the observed change in slope of the E.M.F. / -log x_{PbX_2} plot.

The behaviour of the systems in respect of their values of x_c' leads one to suspect that there may be another factor which influences the stability of the complex ions and the tendency to covalent bond

formation in the melts. It is suggested that a factor which may be important is a tendency for the alkali metal cation not to exist entirely as "free" M^+ entities but to be "associated", to some extent, by ion - pair formation with complex anions. Thus, for example, for the reaction

$$PbX_3^- + M^+ \rightleftharpoons [PbX_3]^- M^+ ,$$

which almost certainly takes place in the molten electrolytes, the equilibrium constant may have appreciable magnitude. Such a process of ion - pair formation would reduce the number of "free" polarising M^+ cations present in the electrolyte, thus stabilising anionic complexes.

The ion - pairing may take place by partial "occlusion" of the M^+ ion within the framework of the complex anion. It is possible that for the systems $PbCl_2$ - CsCl and $PbCl_2$ - RbCl the structures of the complex species present are such that the partial "occlusion" of the M^+ ions, leading to ion - pair formation, can take place more easily with Rb^+ ions than with Cs^+ ions, owing to the smaller radius of Rb^+ compared to that of Cs^+.

Thus, even though the polarising powers of these two ions follow the order $\phi_{Rb^+} > \phi_{Cs^+}$, the number of "free" polarising Rb^+ ions could be substantially less, in a mixture of $PbCl_2$ and RbCl of given composition, than the number of "free" Cs^+ ions in a mixture of $PbCl_2$ and CsCl of the same composition. Hence, covalent bond formation would be inhibited to a greater extent by Cs^+ than by Rb^+ ions. This is a possible explanation of the inversion in the expected order of properties of the two chloride systems, e.g. the fact that in the corres-

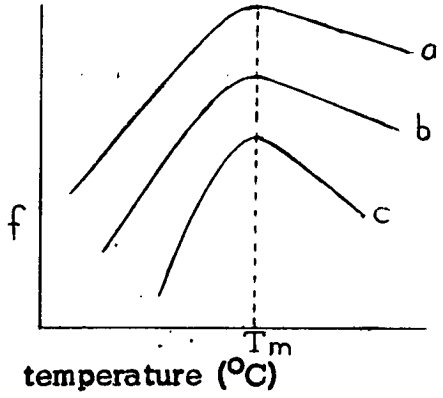
ponding E / -log x_{PbCl_2} plots $(x'_c)_{PbCl_2 - RbCl} > (x'_c)_{PbCl_2 - CsCl}$ and $(x''_c)_{PbCl_2 - RbCl} > (x''_c)_{PbCl_2 - CsCl}$

which is opposite to the expected relative magnitudes of the (x_c). The above considerations also offer an explanation of the facts :

(a) the $PbCl_2$ - RbCl system shows deviations from thermodynamic ideality whihh are approximately equal to, and greater than in some regions of composition, the deviations exhibited by the $PbCl_2$ - CsCl system;

(b) the deviations from additivity of the equivalent conductance of $PbCl_2$ - RbCl mixtures[1] is greater, in some regions of composition, than the deviations shown by the $PbCl_2$ - CsCl system, whereas the reverse relative order of deviations is expected.

Having examined the influence of temperature, proportion of ligand and polarising power of M^+ on the systems PbX_2 - MX, we are now able to predict more completely the dependence of the function f (relative increase in partial vapour pressure of alkali halide) on temperature and melt compositions. The predicted dependence is illustrated below :



(a) { PbX_2 - CsX
{ PbX_2 - RbX
(b) PbX_2 - KX
(c) PbX_2 - NaX

Tm has the same significance as before.

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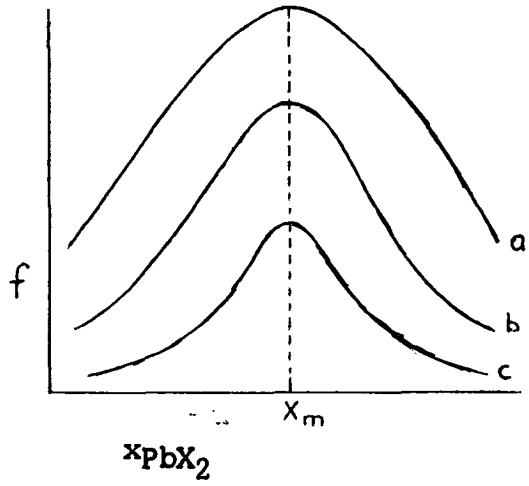
1. Bloom and Mackey, to be published (Trans. Faraday Soc.)



(a) $\begin{cases} PbX_2 - CsX \\ PbX_2 - RbX \end{cases}$
(b) PbX_2 - KX
(c) PbX_2 - NaX

x_m has the same significance as before.

It is suggested that the species PbX_3^- is probably the most important entity in lead halide - alkali halide mixtures, in the sense that it is this species which has the greatest governing influence on the properties of these mixtures. This contention is supported by a variety of experimental evidence as well as by the theoretical considerations outlined above. The E.M.F. / x_{MX} curves (obtained in this work) for the four bromide systems and for the system $PbCl_2$ - CsCl, all show a point of inflexion at the composition corresponding to approximately 50 mole % alkali halide, and the diffusion potential isotherms all exhibit a maximum (or "latent" maximum) in this region of composition.

For the PbX_2 - MX systems in general, there is other experimental evidence for the presence of complex ions. Some of this evidence has been presented in the Introduction (Chapter 1) to this Thesis. Bloom has summarised [1] "molten salt systems in which there is good evidence [2] for the formation of complex ions...". The following table, which is abstracted from Bloom's review, deals only with those systems of the type PbX_2 + MX.

1. Bloom, Pure and Applied Chem., 7, 389 (1963)
2. Bloom, Rev. Pure and Appl. Chem., 9, 139 (1959)

System	Methods of Investigation	Complex ions postulated
$PbCl_2$+KCl	Conductance, molar volume, transport number, surface tension, E.M.F., vapour pressure	$PbCl_3^-$, $PbCl_4^{2-}$, $PbCl_6^{4-}$
$PbCl_2$+RbCl	E.M.F., surface tension, conductance, molar volume	$PbCl_3^-$, $PbCl_4^{2-}$, $PbCl_6^{4-}$
$PbCl_2$+CsCl	Conductance, molar volume	$PbCl_3^-$, $PbCl_4^{2-}$, $PbCl_6^{4-}$

(the references to the various investigations are given by Bloom (loc.cit.)

The species $PbCl_3^-$, $PbCl_4^{2-}$, $PbCl_6^{4-}$, $PbCl^+$, $PbCl_5^{3-}$, $Pb_2Cl_5^-$ [1] and $Pb_2Br_5^-$ [2] appear to be the only complex ions whose presence in melts has previously been postulated for the systems PbX_2 - MX. Other species have been postulated for other systems of the type $M'X_2$ - MX, where M' is a divalent metal, M an alkali metal as before and X a halide. For the systems $ZnCl_2$ - alkali chloride the presence of the ion $Zn_2Cl_7^{3-}$ has been suggested [3], together with $ZnCl^+$ [4].

The present author suggests that in any system of the type $M'X_2$ + MX a large number of different complex ions may exist. Their existence has not hitherto been effectively demonstrated experimentally, because it has previously been found possible to interpret the observed properties of systems e.g. deviations of thermodynamic activity from ideal values, by assuming the presence in the mixtures of only one or perhaps two, complex species. If our postulates concerning the relative strength of bonding in complexes of the type $Pb_x X_y^{(y-2x)-}$ are correct, it is to be

1. Lantratov and Alabyshev, Zh.Prikl.Khim., 26, 263 (1953)
2. Lantratov and Shevlyakova, Russ.J.Inorg.Chem., 4, 523 (1959)
3. Lantratov and Alabyshev; quoted by Watelle-Marion, J.Chim.Phys., 56, 302 (1959).
4. Bues; quoted by Watelle-Marion, J.Chim.Phys., 56, 302 (1959).

expected that only a few complex species - those which are most strongly bound - will be responsible for the greater part of the observed properties of molten salt mixtures. This is supported by the fact that the presence of the complex species PbX_3^- in mixtures PbX_2 - MX has been proposed by many investigators. It is this species which, according to our postulates, is the most strongly covalently bound species in the series of possible $Pb_x X_y^{(y-2x)-}$ complexes.

Phase diagrams for systems PbX_2 - MX have been invoked in discussion of the possible complex species present in the molten mixtures PbX_2 - MX. Thus, on the basis of the appropriate phase diagrams Pletenev and Rosov[1] were led to the conclusion that chemical compounds formed by mixtures and detected by thermal analysis, also exist in the melts in the form of the corresponding complex ions. It cannot be doubted that the structures of molten salt mixtures are related to the structures of the solid mixtures from which they are formed. It is to be emphasised however, that the structure of the solid <u>at the melting point</u> and not at room temperature is the proper basis for comparison of the solid and liquid. Furthermore, conclusions drawn on the basis of the structure of the solid at the melting point, regarding complex species present in the melt could be valid only for temperatures immediately above the melting point. The phase diagram gives no information whatever regarding the structure and constitution of the liquid salt at temperatures much higher than the temperatures at which the solid mixtures melt. Strictly, the phase diagram gives no information concerning the structure of the system at <u>any</u> temperature above the melting point of a solid mixture.

1. Pletenev and Rosov, Zh.Fiz.Khim., 9, 654 (1937)

4. Theoretical Considerations

(i) E.M.F. of the Concentration Cell with Transference containing Molten Electrolyte

Guggenheim[1] defines a concentration cell with transference as follows : "When an electrochemical cell contains only two solutions, one surrounding each electrode, and these two solutions are so nearly alike in composition that they may be regarded as identical except with respect to the reactions at the electrodes, the cell is called a cell without transference. When a current flows through the cell there is in fact necessarily transference of some electrolyte from the one electrode to the other, but if the two electrode solutions are of nearly identical composition the changes in the chemical potentials of the electrolytes transferred are negligible and so this transference is without importance..... Any cell which does not satisfy the conditions in the definition of a cell without transference is called a cell with transference." In the cell with transference thus, the compositions of the two electrolyte solutions are sufficiently different for there to be changes in the chemical potentials of the electrolytes transferred, due to this transfer.

The following treatment of the cells with transference follows that of Guggenheim.[1] Consider the case that the two electrodes are identical so that the chemical processes taking place at the electrodes are the converse of each other. Let us consider the cell

1. Guggenheim, "Thermodynamics", North-Holland, Amsterdam (1957).

$$M \;\Big|\; \underset{\text{Solution I}}{MX_2 + M^1X} \;\Big\vdots\; \underset{\text{SOLUTIONS}}{\text{BRIDGE}} \;\Big\vdots\; \underset{\text{Solution II}}{MX_2 + M^1X} \;\Big|\; M \qquad \ldots I$$

We assume that the liquid junction between the two electrolytes is constituted by bridge solutions in which the composition varies continuously. It is essential to exclude any discontinuity of composition between electrolytes I and II for in such a case the passage of an infinitesimal current would not be reversible and it would not then be feasible to apply thermodynamic equations. There is simultaneously taking place irreversible diffusion between the two solutions, tending to equalise their compositions. It is, however, possible to regard this irreversible diffusion as superposed on the reversible flow of current and the former may be neglected while considering the latter.

The condition of continuity of composition is the only condition imposed on the nature of the bridge solutions. In view of this condition the compositions of the outermost bridge solutions are identical with those of the electrode solutions. If the bridge solutions are formed by natural mixing or inter-diffusion of the two electrode solutions, then their compositions throughout will be intermediate between those of the two electrode solutions. The formulae to be derived are applicable to all cases, but we consider first the elementary cell

$$M \;\Big|\; \underset{x}{MX_2} + M'X \;\Big\vdots\; \underset{(x+dx)}{MX_2} + M'X \;\Big|\; M \qquad \ldots II$$

Solution I Solution II

where the two electrode solutions differ only infinitesimally in composition; x denotes the mole fraction of MX_2 in the molten salt solution.

Even in the elementary cell II there is not thermodynamic equilibrium and there is initially a state of interdiffusion between the two solutions. It is necessary therefore to invoke some assumptions extraneous to classical thermodynamics (which applies strictly only to equilibrium conditions.) We make, in the first instance, the simplest (but not the least restrictive) assumption which leads to correct conclusions. The same conclusions can be reached by a less restrictive assumption (see later). We assume that the flow, J_i, of the ionic species i is directly proportional to its gradient of chemical potential, μ_i. We may, for simplicity and without loss of generality, assume that the gradients are in the y-direction. The assumption thus becomes

$$J_i = - L_i \cdot \frac{d\mu_i}{dy} \qquad \ldots(1)$$

where the proportionality constant L_i may depend on the compositions of the solutions but is independent of the gradient of composition and independent of the flow. We consider the condition of zero electric current which exists when the cell circuit is open or when the cell is exactly balanced against a potentiometer. At each electrode we have the equilibrium

$$M^{2+} + 2\,e^- \rightleftharpoons M \qquad \ldots(2)$$

If Z_i is the charge on ion i, the free energy change associated with this reaction is, generally

$$dG = \frac{1}{Z_{M^{z+}}} \cdot d\mu_{M^{z+}} = \frac{1}{Z_{M^{2+}}} \cdot d\mu_{M^{2+}} \qquad \ldots(3)$$

The value of Z is of course 2, in this case, but it is useful, at this stage

not to insert the numerical value. The electromotive force of cell II is therefore given by

$$- F \, dE_t = \frac{1}{Z_{M^{2+}}} \, d\mu_{M^{2+}} \qquad \ldots(4)$$

since

$$dG = - FdE_t \qquad \ldots(5)$$

where E_t denotes the E.M.F. of the cell with transference. Equation (4) may be written as

$$- F \frac{dE_t}{dy} = \frac{1}{Z_{M^{2+}}} \frac{d\mu_{M^{2+}}}{dy} \qquad \ldots(6)$$

The condition for zero electric current flow is

$$\sum_i Z_i J_i = 0 \qquad \ldots(7)$$

Substituting (1) into (7) we have

$$- \sum_i Z_i L_i \frac{d\mu_i}{dy} = 0 \qquad \ldots(8)$$

We now multiply (6) by $\sum_i Z_i^2 L_i$ and add (8), obtaining

$$- \sum_i Z_i^2 L_i F \frac{dE_t}{dy} = \sum_i Z_i^2 L_i \left(- \frac{1}{Z_i} \frac{d\mu_i}{dy} + \frac{1}{Z_{M^{2+}}} \frac{d\mu_{M^{2+}}}{dy} \right) \qquad \ldots(9)$$

and consequently

$$-F \, dE_t = \frac{\sum_i Z_i^2 L_i \left(- \frac{1}{Z_i} d\mu_i + \frac{1}{Z_{M^{2+}}} d\mu_{M^{2+}} \right)}{\sum_i Z_i^2 L_i} \qquad \ldots(10)$$

Equation (10) is a complete and unambiguous formula for the E.M.F. in terms of the quantities L_i defined in assumption (1). We can transform the expression on the right of (10) into a more tractable form

by considering the different condition where the two electrode solutions are identical and an external potential difference dE_t^e is applied across the electrodes. Under these conditions we have

$$-FdE_t^e = \frac{1}{Z_i} \quad d\mu_i \quad \text{(for all i)} \qquad \ldots(11)$$

Hence, according to (11)

$$J_i = Z_i \; L_i \; F \frac{d\, E_t^e}{dy} \qquad \text{(for all i)} \qquad \ldots(12)$$

and the electric current per unit cross-section carried by the ionic species i will be

$$Z_i \; F \; J_i = Z_i^2 \; L_i \; F^2 \; \frac{dE_t^e}{dy} \qquad \ldots(13)$$

The fraction of the total current carried by the ionic species i – the transport number of the species i – is then given by

$$t_i = \frac{Z_i^2 \; L_i}{\sum_i Z_i^2 L_i} \qquad \ldots(14)$$

Comparing (10) with (14) we deduce

$$-F\, dE_t = \sum_i t_i \left(-\frac{1}{Z_i} \; d\mu_i + \frac{1}{Z_{M^{2+}}} \; d\mu_{M^{2+}} \right) \qquad \ldots(15)$$

Returning now tc cell I it is apparent that this cell may always be regarded as several cells of type II in series, all electrodes other than the two extreme ones cancelling in pairs. We accordingly deduce from (15) for the E.M.F. of cell I

$$-FE_t = \int \sum_i t_i \left(-\frac{1}{Z_i} \; d\mu_i + \frac{1}{Z_{M^{2+}}} \; d\mu_{M^{2+}} \right) \qquad \ldots(16)$$

We may rewrite (16) in terms of absolute activities as

$$E_t = -\frac{RT}{F} \int \sum_i t_i \left(-\frac{1}{Z_i} \; d\ln a_i + \frac{1}{Z_{M^{2+}}} \; d\ln a_{M^{2+}} \right) \qquad \ldots(17)$$

We have derived expressions for the E.M.F. of the concentration cell with transference with two identical electrodes. The accurate expressions for the E.M.F. of the most general type of cell with transference have been formulated by Taylor[1].

We shall now apply the formulae derived above to a specific molten salt concentration cell, of the type investigated in the present work. We consider the cell

$$\begin{array}{c|c|c|c|c} & \text{electrolyte I} & \vdots & \text{electrolyte II} & \\ Pb & PbX_2 + MX & \vdots & PbX_2 + MX & Pb \\ & x_1 & \vdots & x_{11} & \end{array} \qquad \ldots III$$

X = Cl or Br, M = Na, K, Rb or Cs. x_1 and x_{11} are the mole fractions of PbX_2 in the two electrolytes 1 and 11. The E.M.F. of cell III is given by (assuming that the electrolytes are completely dissociated into Pb^{2+}, M^+ and X^- ions)

$$E_t = -\frac{RT''}{F'}\int \Sigma_i t_i \left(-\frac{1}{Z_i} d\ln a_i + \frac{1}{Zp_b 2+} d\ln a_{Pb^{2+}} \right) \qquad \ldots(18)$$

where the integration extends through all the bridge solutions from the left electrode solution (electrolyte 1) to the right electrode solution (electrolyte 11). On expanding (18) we obtain

$$E_t = \frac{RT''}{F'}\int \left(-\frac{t_{M^+}}{Z_{M+}} d\ln a_{M^+} + \frac{t_{M^+}}{Zp_b 2+} d\ln a_{Pb^{2+}} - \frac{t_X}{Z_{X-}} d\ln a_{X^-} + \frac{t_X}{Z_{Pb2+}} d\ln a_{Pb^{2+}} \right)$$

Inserting the numerical values of the Z_i, and using the relationship

$t_{X^-} = 1 - tp_b 2+ - t_{M^+}$ (since $\sum_i t_i = 1$), we obtain

$$E_t = -\frac{RT''}{F'}\int - t_{M^+} d\ln a_{M^+} + \frac{1}{2} t_{M^+} d\ln a_{Pb^{2+}} + d\ln a_{X-} - t_{M^+} d\ln a_{X^-}$$

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1. Taylor, J. Physic Chem., 31, 1478 (1927)

$$-t_{Pb^{2+}} \, d \ln a_{X^-} + \frac{1}{2} \, d \ln a_{Pb^{2+}} - \frac{1}{2} \, t_{M^+} \, d \ln a_{Pb^{2+}} - \frac{1}{2} \, t_{Pb^{2+}} \, d \ln a_{Pb^{2+}} \Big)$$

We make use now of the relationships *

$$a_{MX} = a_{M^+} \cdot a_{X^-} \qquad \ldots(19)$$

$$a_{PbX_2} = a_{Pb^{2+}} \cdot a^2_{X^-} \qquad \ldots(20)$$

We obtain thence

$$E_t = -\frac{RT''}{F'} \int \left(-t_{M^+} \, d \ln a_{MZ} - \frac{1}{2} \, t_{Pb^{2+}} \, d \ln a_{PbX_2} + \frac{1}{2} \, d \ln a_{PbX2} \right)$$

i.e.

$$E_t = -\frac{RT''}{F'} \int \left[\frac{1}{2} \left(1 - t_{Pb^{2+}} \right) d \ln a_{PbX_2} - t_{M^+} \, d \ln a_{MX} \right] \qquad \ldots(21)$$

We apply now the Gibbs - Duhem relationship, in the form

$$d \ln a_{MX} = - \frac{x_{PbX_2}}{x_{MX}} \, d \ln a_{PbX_2} \qquad \ldots(22)$$

(x_{PbX_2} and x_{MX} are the mole fractions of PbX_2 of PbX_2 and MX respectively in the molten salt electrolyte). Combination of (21) and (22) yields

$$E_t = - \frac{RT''}{2 F'} \int \left[d \ln a_{PbX_2} \left(\frac{x_{MX} - t_{Pb^{2+}} \, x_{MX} + 2 t_{M^+} \, x_{PbX_2}}{x_{MX}} \right) \right] \qquad \ldots(23)$$

which is the desired relationship for the E.M.F. of cell III.

It must be emphasised, in connection with equation (23) above, that the validity of this equation depends entirely on the validity of the structural model we have assumed for the electrolyte, and on the correctness of the electrode processes assumed. In general, for other models of the electrolyte, different equations for the cell E.M.F. apply. This point is discussed in more detail below.

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* These relationships are discussed in detail in a later section, in reference to diffusion potential (see Section D4 (iii) of this chapter).

(ii) Determination of Transport Numbers

Let us consider in detail equation (23) for the E.M.F. of the concentration cell with transference. For any composition of electrolyte, i.e. for any known values of x_{MX} (and therefore x_{PbX_2}) both the E.M.F., E_t, and the activity of lead halide, a_{PbX_2}, are measurable quantities. It is evident therefore, that provided the variation of the t_i with $\ln a_{PbX_2}$ were known, it would in principle be possible to calculate a function relating to the ionic transport numbers. Unfortunately this is not possible in practice, because the relationship between t_i and $\ln a_{PbX_2}$ is not known, at least for the systems PbX_2 - MX.

Another approach to the determination of the transport numbers is as follows: Consider the infinitesimal change in cell E.M.F., $d E_t$, accompanying an infinitesimal change in $\ln a_{PbX_2}$, namely $d \ln a_{PbX_2}$. Accordingly, from (23) we obtain :

$$\frac{d E_t}{d \ln a_{PbX_2}} = - \frac{RT}{2F} \left(1 - t_{Pb^{2+}} + 2t_{M^+} \frac{x_{PbX_2}}{x_{MX}} \right) \qquad \ldots(24)$$

Consider now the infinitesimal change, dE, in the E.M.F. of the corresponding cell without transference, accompanying an infinitesimal change, $d \ln a_{PbX_2}$, in $\ln a_{PbX_2}$. We have

$$E = - \frac{RT}{2F} \int d \ln a_{PbX_2} \qquad \ldots(25)$$

so that

$$\frac{dE}{d \ln a_{PbX_2}} = - \frac{R T}{2F} \qquad \ldots(26)$$

Combining (24) and (26) we obtain

$$\frac{dE_t \;/\; d\ln a_{PbX_2}}{dE \;/\; d\ln a_{PbX_2}} = \left(1 - t_{Pb^{2+}} + 2t_{M^+} \frac{x_{PbX_2}}{x_{MX}}\right) \qquad \ldots(27)$$

Thus, according to equation (27), from plots of E_t and E against $\ln a_{PbX_2}$ or from a plot of E_t against E, we may calculate from the slopes of the plots, the values of the function expressed by

$$T = 1 - t_{Pb^{2+}} + 2t_{M^+} \frac{x_{PbX_2}}{x_{MX}}$$

at any composition. Unfortunately the function T involves two interdependent transport numbers, and without an independent relationship between t_{M^+} and $t_{Pb^{2+}}$ it is not possible to deduce the value of either of these transport numbers.

It is possible, however, to proceed a little further. For pure lead halide, t_{M^+} must, of course, vanish. Hence by extrapolating the function T to the composition corresponding to pure lead halide, it may be possible to deduce the values of the ionic transport numbers in the pure lead halide. We shall, accordingly, examine the composition dependence of the function T. Let us express T as the sum of two separate functions, namely

$$T = \left(1 - t_{Pb^{2+}} - 2t_{M^+}\right) + \left(\frac{2t_{M^+}}{x_{MX}}\right) = T_1 + T_2 \qquad \ldots(28)$$

(Where we have utilised the relationship $x_{PbX_2} + x_{MX} \equiv 1$). At the composition given by $x_{MX} = 0$ (i.e. pure lead halide) the value of T_1 is given by

$$T_1 = 1 - t_{Pb^{2+}} = t_{X^-} \qquad \ldots(29)$$

At the same composition, the value of T_x is evidently indeterminate (0 / 0). Thus we must consider the limit of the function T, as $x_{MX} \rightarrow 0$. We write

$$1 = \underset{x_{MX} \rightarrow O}{\text{Limit}} \frac{dE_t / d \ln a_{PbX_2}}{dE / d \ln a_{PbX_2}} = \underset{x_{MX} \rightarrow O}{\text{Limit}} \frac{dE_t}{dE} \qquad \ldots(30)$$

$$= l_1 + l_2 ,$$

where

$$l_1 = \underset{x_{MX} \rightarrow O}{\text{Limit}} \left(1 - t_{Pb^{2+}} - 2t_{M+} \right)$$

$$l_2 = \underset{x_{MX} \rightarrow O}{\text{Limit}} \left(\frac{2t_{M+}}{x_{MX}} \right) \qquad \ldots(31)$$

According to equation (29), $l_1 = t_{X^-}$. The crucial point is the value of the limit l_2 . It is not possible, in principle, to calculate l_2 , because the functional relationship between t_{M^+} and x_{MX} is not known. If t_{M+} were, for example, a quadratic or higher function of x_{MX} , then $l_2 = 0$, and $1 = t_{X^-}$. We may assert that in general if and only if t_{M+} is a function, $f(x_{MX})$, of x_{MX} such that

$$\frac{dt_{M+}}{dx_{MX}} = f^1 (x_{MX}) \qquad \ldots(32)$$

then $l_2 = 0$, and it is possible to determine the ionic transport numbers in pure fused lead halide.

We conclude generally, therefore, that it is possible to determine transport numbers in pure fused salts from the E.M.F's of appropriate

concentration cells, provided the functional dependence of the transport number of diluent metal cation on mole fraction of diluent salt is known. By diluent salt we mean the salt which is not derived from the electrode metal.

We shall now reiterate the discussion - in sections 4, (i) and (ii)(above) - of the cell with transference, on the basis of a different structural model for the electrolyte. Let us assume that the mixture $PbX_2 + MX$ is dissociated into PbX^+, M^+ and X^- ions, in which case the electrodes are presumably reversible with respect to PbX^+ ions. Equation (18) becomes

$$E_t = -\frac{RT''}{F'}\left(\sum_i t_i \left(-\frac{1}{Z_i} d \ln a_i + \frac{1}{Z_{PbX^+}} d \ln a_{PbX^+} \right) \right)$$

$$= -\frac{RT''}{F'}\left(\left(-t_{M+} d \ln a_{M+} + t_{M+} d \ln a_{PbX^+} + t_X d \ln a_{X^-} \right. \right.$$

$$\left. \left. + t_X - d \ln a_{PbX^+} \right) \right) \quad \ldots(33)$$

We make the substitution

$$t_{X^-} = 1 - t_{PbX^+} - t_{M+} \quad \ldots(34)$$

yielding, from (33) and (34)

$$E_t = -\frac{RT''}{F'}\left(\left(-t_{M+} d \ln a_{M+} + t_{M+} d \ln a_{PbX^+} + d \ln a_{X^-} - t_{PbX^+} d \ln a_{X^-} \right. \right.$$

$$\left. \left. - t_{M+} d \ln a_{X^-} + d \ln a_{PbX^+} - t_{PbX^+} d \ln a_{PbX^+} - t_{M+} d \ln a_{PbX^+} \right) \right)$$

Since

$$a_{MX} = a_{M^+} \cdot a_{X^-} \quad \text{(equation (19))}$$

and

$$a_{PbX_2} = a_{PbX^+} \cdot a_{X^-} \qquad \ldots(35)$$

we obtain (from (34), (19) and (35))

$$E_t = - \frac{RT''}{F'} \int \left[\left(1 - t_{PbX^+} \right) \; d \ln a_{PbX_2} - t_{M+} \, d \ln a_{MX} \right]$$

Application of the Gibbs - Duhem equation (equation 22) gives

$$E_t = - \frac{RT''}{F'} \int \left(1 - t_{PbX^+} + t_{M+} \frac{x_{PbX_2}}{x_{MX}} \right) d \ln a_{PbX_2} \qquad \ldots(36)$$

We may write the equation analogous to equation (28) , namely

$$T = \left(1 - t_{PbX^+} - t_{M+} \right) + \left(\frac{t_{M+}}{x_{MX}} \right) \qquad \ldots(37)$$

Expressing the limits, 1, as before, we have

$$1 = \underset{x_{MX} \to 0}{\text{Limit}} \; \frac{dE_t / d \ln a_{PbX_2}}{d E / d \ln a_{PbX_2}} = l_1 + l_2$$

where

$$l_1 = \underset{x_{MX} \to 0}{\text{Limit}} \left(1 - t_{PbX^+} - t_{M+} \right)$$

$$l_2 = \underset{x_{MX} \to 0}{\text{Limit}} \left(\frac{t_{M+}}{x_{MX}} \right) \qquad \ldots(38)$$

it follows that if $l_2 = 0$, then $l_1 = 1 - t_{PbX^+} = t_{X^-}$

In general, we conclude that the ion whose transport number may be determined, in principle (provided sufficient information is known), is that ion - of the salt derived from the electrode metal - with respect to which the electrodes are <u>not reversible</u>. Thus, let us re-examine the model above, assuming that the electrodes are reversible

with respect to X^- ions. In that case, the transport number of the PbX^+ ion is the transport number which is specified by the limit l_1. If the electrolyte were completely dissociated into Pb^{2+}, M^+ and X^- ions, and if the electrodes were reversible with respect to X^- ions, then the transport number $t_{Pb^{2+}}$ is specified by the limit l_1 .

The Definition of Transport Numbers in Molten Salt Mixtures.

In the discussion of diffusion potentials (which follows in 4 (iii)) we shall require general expressions for the ionic transport numbers in salt mixtures of the type PbX_2 + MX. Since the appropriate relationships do not appear to have been previously published (to the author's knowledge), it seems appropriate to outline the derivation of the relevant formulae.

In the molten salt mixture PbX_2 + MX, let us denote the mole fraction of lead halide by x, and assume that the electrolyte is completely dissociated into simple ions (i.e. Pb^{2+} , M^+ and X^-). To avoid tedious repetition, we shall signify the species Pb^{2+} by the subscript 1, M^+ by 2 and X^- by 3. Consider a volume V (litres) of electrolyte. If the number of moles of mixture present is m, and if the molar volume of the mixture is V_m , then the numbers of gram - ions of the various ionic species present in the electrolyte are given by

$$n_1 = mx$$

$$n_2 = m(1 - x)$$

$$n_3 = 2mx + m(1 - x) \qquad \ldots(52)$$

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The molar concentrations of the various species are, therefore

$$C_1 = mx / V = mx / mV_m = x / V_m$$

$$C_2 = (1 - x) / V_m$$

$$C_3 = m(2x + 1 - x) / mV_m = (x + 1) / V_m \quad \ldots(40)$$

In general, the transport number of an ion i is given by

$$t_i = \frac{K_i}{\sum_i K_i} \quad \ldots(41)$$

where K_i is the specific conductance due to ion i. Using the relationship

$$\bar{\lambda}_i = \frac{1000\ K_i}{c_i} \quad \ldots(42)$$

where $\bar{\lambda}_i$ is the molar conductance due to ion i and c_i is the "molar" concentration of i, we have

$$t_i = \frac{\bar{\lambda}_i\ c_i}{\sum_i \bar{\lambda}_i\ c_i} \quad \ldots(43)$$

Since

$$\bar{\lambda}_i = z_i\ F\ u_i \quad \ldots(44)$$

where z_i is the charge carried by ion i and u_i is its mobility ($u_i < O$ for anions and $> O$ for cations), therefore

$$t_i = \frac{z_i\ u_i\ c_i}{\sum_i z_i\ u_i\ c_i} \quad \ldots(45)$$

Now, $z_1 = 2$, $z_2 = 1$ and $z_3 = -1$. Thus combination of (40) and (45) yields

$$t_1 = \frac{2\ u_1 \left(\frac{x}{V_m}\right)}{2\ u_1\left(\frac{x}{V_m}\right) + u_2\left(\frac{1 - x}{V_m}\right) - u_3\left(\frac{1 + x}{V_m}\right)} \quad \ldots(46)$$

and the corresponding equations for t_2 and t_3 . On simplification we obtain

$$t_1 = \frac{2\,u_1\,x}{2\,u_1\,x + u_2\,(1-x) - u_3\,(1+x)}$$

$$t_2 = \frac{u_2\,(1-x)}{2\,u_1\,x + u_2\,(1-x) - u_3\,(1+x)}$$

$$t_3 = \frac{-\,u_3\,(1+x)}{2\,u_1\,x + u_2\,(1-x) - u_3\,(1+x)} \qquad \ldots(47)$$

which are the required relationships.

(iii) The Diffusion Potential

The treatment of diffusion potential presented below follows, in part, that of Mac Innes[1].

Consider two molten electrolytes brought into contact in a region in which the composition varies from that of one of the electrolytes to that of the other electrolyte. The composition distribution depends on rates of diffusion, convection, mixing etc. However, it is possible to divide the intermediate region into laminae, of such dimensions that in any one lamina the composition gradient across the lamina is indefinitely small. Let one such lamina be AB below, on one side (A) of which is an electrolyte

x_1 ‖ $x_1 \pm dx_1$ containing the ions 1, 2, ...i, ...n, whose

x_i ‖ $x_i \pm dx_i$ ion fractions* are $x_1 \cdots x_i \ldots x_n$. On the

x_n ‖ $x_n \pm dx_n$ other side of the lamina the ion - fractions

A B

are $x_1 \pm dx_1$, ... , $x_n \pm dx_n$. Let the charges carried by the ions be z_1 , ... z_n , z_i being given by $\pm n_i e$, where n_i is the number of charges and e the electronic charge; z_i includes the sign of the charge. Further suppose that the transport numbers of the ions are t_1 , ..., t_n . Motion of the ions in the boundary layer will cause a potential difference, $d\mathcal{E}$, to be established across the layer.

If one Faraday of current passes from A to B, then (t_i / z_i) gram ions of each ion will pass through the layer. Passage of

1. Mac Innes, "The Principles of Electrochemistry", Dover, New York (1961).

* We define x_i as the ratio of the number of gram ions of species i to the total number of gram ions of all the ions present in the electrolyte.

ions will be from left to right for ions with positive z, and from right to left for ions with z negative. The total change of Gibbs free energy, dG, accompanying this process will be

$$dG = \sum_n \frac{t_i}{z_i} \, d\mu_i \qquad \ldots(48)$$

where μ_i is the chemical potential of ion i. Since

$$\sum_n t_i = 1 \qquad \ldots(49)$$

and

$$-\Delta G = zFE \qquad \ldots(50)$$

we have

$$d\mathcal{E} = -\frac{RT}{F} \sum_n \frac{t_i}{z_i} \, d \ln a_i \qquad \ldots(51)$$

where we have used the relationship

$$\mu_i = \mu_i^{\circ} + RT \ln a_i \qquad \ldots(52)$$

Any liquid junction between the two electrolytes 1 and 11 will consist of an indefinite number of thin laminae, and the potential across the liquid junction will therefore be given by

$$\mathcal{E} = -\frac{RT''}{F'} \int \sum_n \frac{t_i}{z_i} \, d \ln a_i \qquad \ldots(53)$$

In the derivation of this equation we have made two non-thermodynamic assumptions, in as much as neither the single potential of a liquid junction nor the individual ion activities can be measured. The use of these non-thermodynamically defined quantities has been justified by Mac Innes [1] (for the case of (aqueous) solutions of electrolytes) and

1. Mac Innes, "The Principles of Electrochemistry", Dover, New York (1961).

by Laity[1] (for the case of molten electrolytes). Mac Innes[2] states "..,This equation [equation (53)] is not rigorously thermodynamic since neither the single potential of a liquid junction nor the ion activities, a_i, can be measured. However, ...correct thermodynamic equations are obtained if this equation is combined with equations for electrode processes in such a manner as to include the processes for a complete galvanic cell. In such cases it will always be possible to combine the single ion activities into physically measurable mean ionic activities." For the case of the molten electrolyte, it will always be possible, by defining the activity of a neutral component (a measurable quantity) by relations such as

$$a_{M_n X_m} = a^n_{M^{m+}} \cdot a^m_{X^{n-}} \quad , \qquad \ldots(54)$$

to express the ion activities in terms of thermodynamically defined quantities.

In order to integrate the fundamental differential equation for diffusion potential equation (53) , certain assumptions must be made. Several integrations of equation (53) have been performed, notably by Henderson [3] and Planck[4].

We shall consider molten salt concentration cells of the general type

$$\text{Pb} \;\big|\; \underset{\text{PbX}_2 + \text{MX}}{\text{electrolyte 1}} \;\big\vdots\; \underset{\text{PbX}_2 + \text{MX}}{\text{electrolyte 11}} \;\big|\; \text{Pb} \qquad \ldots \text{I}$$

The compositions of the two electrolytes (which are, in practice, separated by a porous disc) are specified by the appropriate ion fractions x_i' and x_i''. For concentration cells of this type, it seems that the assumption of a "continuous - mixture" type liquid junction is more realistic than the assumption of a "constrained - diffusion" type. We shall, accordingly, employ the Henderson equation for the diffusion potential in discussion of cells of type I.

In the present work, the diffusion potential has been evaluated

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1. Laity, in "Reference Electrodes", editors Ives & Janz, Chapter 12, Adademic Press, New York (1961).
2. MacInnes, "The Principles of Electrochemistry", Dover, New York (1961)
3. Henderson, Z.physik.Chem., 59, 118 (1907); 63, 325 (1908)
4. Planck, Ann. physik., 3, 33, 161 (1890); 3, 40, 561 (1890)

for cells which are a special case of cell I, namely

$$\mathrm{Pb} \;\Big|\; \underset{\text{pure}}{\overset{\text{electrolyte 1}}{\mathrm{PbX_2}}} \;\Big\|\; \overset{\text{electrolyte 11}}{\mathrm{PbX_2 + MX}} \;\Big|\; \mathrm{Pb} \qquad \ldots\text{II}$$

and hence we shall deal specifically with this special case. In the discussion which follows, we shall assume that individual ion activity coefficients, f_i , are unity, so that we may everywhere replace activities a_i by ion - fractions x_i . For cell II above, the ion - fractions x_i may be expressed in terms of the mole fractions of the component salts constituting the electrolytes. To this point, it has not been necessary to specify the ionic species present in the electrolyte, and consequently we have not been obliged to postulate a structural model of the electrolyte, since the treatment has been valid for any structural model. For further detailed discussion however, we must make some assumptions concerning the nature of the species present and in the first instance, we shall assume that the electrolytes $PbX_2 + MX$ and pure PbX_2 are completely dissociated into the simplest ions, i.e. into Pb^{2+}, M^+ and X^- ions. In that case, the ion - fractions of the various ionic species present in the electrolytes are given by :

$$x'_{Pb^{2+}} = 1, \quad x'_{M+} = 0, \quad x'_{X^-} = 2x'_{Pb^{2+}} = 2$$

$$x''_{M+} = 1 - x''_{Pb^{2+}}, \quad x''_{X^-} = 2x''_{Pb^{2+}} + x''_{M+} = x''_{Pb^{2+}} + 1 \qquad \ldots(55)$$

For simplicity, let us signify the entity Pb^{2+} by subscript 1, M^+ by 2 and X^- by 3, and denote the mole-fraction of PbX_2 in electrolyte 11 by x. Then $x''_{Pb^{2+}} = x$, etc.

Our Principal object now is to relate explicitly the diffusion potential to the transport properties of the ionic species constituting the electrolytes. We shall first investigate the conditions for which $\mathcal{E} = 0$.

Conditions for zero diffusion potential.

We return to the equations for the E.M.F's of the concentration cells with and without transference. By (24) and (26) we have

$$dE_t = - \frac{RT}{2F} \left[1 - t_1 + 2t_2 \left(\frac{x}{1-x} \right) d \ln a \right]$$

and

$$dE = - \frac{RT}{2F} d \ln a$$

where t_1 denotes the transport number of Pb^{2+} ions, t_2 the transport number of M^+ ions (and t_3 will denote the transport number of X^- ions) and a denotes the activity of lead halide, a_{PbX_2}, in electrolyte II. The diffusion potential is expressed by the relationship

$$d \mathcal{E} = dE_t - dE \qquad \ldots(56)$$

and hence a condition for $\mathcal{E} = 0$ is

$$dE_t = dE \qquad \ldots(57)$$

i.e.

$$1 - t_1 + 2t_2 \left(\frac{x}{1-x} \right) = 1$$

Hence

$$\frac{t_1}{2t_2} = \frac{x}{1-x} \qquad \ldots(58)$$

Equation (58) becomes, using equations (47) to express t_i in terms of mobilities u_i, on simplification

$$u_1 = u_2 \qquad \ldots(59)$$

This is a very important equation [1]; in words, the diffusion potential vanishes if the two cations have equal mobilities in the molten electrolyte.

Let us now examine the consequences of the adoption of a different structural model; specifically, assume the electrolyte to be dissociated into PbX^+, X^- and M^+ ions. Reiterating equation (36) on the basis of this model, we obtain for the E.M.F. of the cell

$$E_t = -\frac{RT''}{F}\int\left[1 - t_1 + t_2\left(\frac{x}{1-x}\right) d \ln a\right] \qquad \ldots(60)$$

in which we have denoted the species PbX^+ by subscript 1, M^+ by 2 and X^- by 3. The condition for $\mathcal{E} = 0$ arising from this equation is

$$\frac{t_1}{t_2} = \frac{x}{1-x} \qquad \ldots(61)$$

The transport numbers t_i are readily defined in terms of the ionic mobilities. The relevant relationships are

$$t_1 = \frac{u_1 x}{s^1}$$

$$t_2 = \frac{u_2 (1-x)}{s^1}$$

$$t_3 = \frac{-u_3}{s^1} \qquad \ldots(62)$$

where s^1 is given by

$$s^1 = u_1 x + u_2 (1-x) - u_3$$

Combining (61) and (62) we find

$$u_1 = u_2$$

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1. This condition for $\mathcal{E} = 0$ has also been expressed by Laity, J.Amer.Chem.Soc., 79, 1849 (1957)

Conditions for non-zero diffusion potential.

Honig[1] has derived, for the case of a binary electrolyte completely dissociated into 2 cations, 1 and 2, and anion 3, the expression

$$\mathcal{E} = -RT \int \frac{1}{(z_1 N_2 + z_2 N_1)} \frac{u_1 - u_2}{\Lambda} \, d N_1 \qquad \ldots(63)$$

in which z_i = charge carried by ion i ($z_i < 0$ for anions),

N_i = equivalent ionic fraction of ion i,

u_i = mobility of ion i ($u_i < 0$ for anions),

Λ = equivalent conductance of mixture.

In the derivation of (63) it was assumed that all ionic activity coefficients have the value unity. Writing equation (63) in the differential form we obtain

$$d\mathcal{E} = -RT \left[\frac{1}{(z_1 N_2 + z_2 N_1)} \frac{u_1 - u_2}{\Lambda} \right] dN, \qquad \ldots(64)$$

From (64) it is apparent that a condition for $\mathcal{E} = 0$ is

$$u_1 = u_2$$

The Variation of Diffusion Potential with Temperature and Composition of the Electrolyte.

Consider the fundamental equation for diffusion potential

$$\mathcal{E} = -\frac{RT}{F} \int \sum_n \frac{t_i}{z_i} \, d \ln a_i \qquad \text{(equation (53))}$$

making the substitution

$$t_i = \frac{z_i c_i u_i}{\sum_n z_i c_i u_i}$$

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1. Honig, Thesis, Amsterdam (1964)

where c_i is the molar concentration of species i, we obtain

$$\mathcal{E} = -\frac{RT''}{F'}\int \frac{\sum_n c_i u_i}{\sum_n z_i c_i u_i} \, d \ln a_i \qquad \ldots(65)$$

Thus the rate of change of diffusion potential with temperature must be a function of both the rate of change of mobility with temperature and the rate of change of ionic activity with temperature, i.e.

$$\frac{d\mathcal{E}}{dT} = \oint \left(\frac{du_i}{dT} \, , \quad \frac{d \ln a_i}{dT} \right) \qquad \ldots(66)$$

At the present time the functional relationships between ionic mobility and temperature, and between ionic activity and temperature are not known. Hence itis not possible to express explicitly and thereby evaluate such differentials as $\frac{du_i}{dT}$ and $\frac{d \ln a_i}{dT}$ and hence to evaluate $\frac{d\mathcal{E}}{dT}$.

Conversely, from the observed temperature dependence of $\mathcal{E}$ it is not possible, at present, to deduce information regarding u_i and a_i. We are able, therefore, to draw only speculative conclusions from the experimental $\mathcal{E}$ / T data, concerning the nature of the species present in the molten electrolyte.

Similar considerations apply to the composition dependence of diffusion potential; terms such as $\frac{du_i}{dx}$ and $\frac{d \ln a_i}{dx}$ cannot be expressed explicitly.

There is a further conceptual difficulty. In principle a_i is not measurable - it is possible to measure only neutral salt activities. If we make use of the relationship

$$a_{M_\alpha X_\beta} = a_M^{\alpha +} \cdot a_X^{\beta -} \qquad \ldots(67)$$

then provided $\frac{da_{M_\alpha X_\beta}}{dT}$ and $\frac{da_{M_\alpha X_\beta}}{dx}$ are known (and there is sufficient data available to evaluate these terms for many molten salt systems) we are able to evaluate the differentials

$$\frac{d}{dT}\left(a_M^{\alpha +} \cdot a_X^{\beta -}\right) \quad \text{and} \quad \frac{d}{dx}\left(a_M^{\alpha +} \cdot a_X^{\beta -}\right)$$

We have now two possible alternative procedures. In the first place

we may assume that all ionic activity coefficients are unity, in which case the ionic activities in the preceeding differentials are replaced by ion-fractions. This is the procedure which is utilised in the Henderson integration of the fundamental equation for diffusion potential. For molten salt mixtures whose behaviour approximates to ideal solution behaviour this procedure should be a good approximation. However, for all mixtures of the type PbX_2 - MX there are significant deviations from thermodynamic ideality and the procedure above is certainly not a valid approximation.

The second possible procedure is the adoption of one of the a_i as a standard of ionic activity and expression of all other a_i with reference to the standard, by utilising known values for the neutral salt activities. This procedure, although being in theory the most useful one, has several serious disadvantages. Provided that all the ionic species present in the melt are identified, we must <u>arbitrarily</u> select one of the ions, say s, and assign to its activity an <u>arbitrary</u> value, say a_s^o. We may, for example, select the alkali metal cation and assign to its activity the value x_{M+} where x_{M+} is the ion-fraction of the ion. This is equivalent to the proposition $f_{M+} = 1$, at all compositions, where f_{M+} is the ionic activity coefficient of the M+ ion. Now, the remainder of the a_i follow from the measured values for a_{MX} and a_{PbX_2}. Although the alkali metal cation probably exists as such to a large extent in the molten electrolyte, it is by no means certain that its activity coefficient will be unity. Nevertheless this procedure involves a considerable reduction in arbitrariness from the assumption $f_i = 1$ <u>for all i</u>. At

the present time there appears to be no less arbitrary procedure and we conclude that in order to calculate terms such as $\frac{d \ln a_i}{dT}$ and $\frac{d \ln a_i}{dx}$ it is necessary to use such a procedure.

Let us consider possible approaches to the evaluation of the differentials $\frac{du_i}{dT}$ and $\frac{du_i}{dx}$. We must point out, first, that for systems PbX_2 - MX very few u_i have been measured; for those systems investigated in this work no u_i have been measured (to the author's knowledge). The mobility of an ion in a molten electrolyte will presumably depend on, inter alia, it s mass, charge and effective radius. As a first approximation, therefore, let us write

$$u_i = f'(m_i, z_i, r_i). \qquad \ldots(68)$$

where f' is an explicit function. There is an immediate simplification possible, in consideration of $\frac{du_i}{dT}$ and $\frac{du_i}{dx}$. Both m_i and z_i must be invariant with respect to temperature and composition and hence the variations of r_i with temperature and composition are the important factors in determining $\frac{du_i}{dT}$ and $\frac{du_i}{dx}$. Intuitively, it would be expected that both $\frac{dr_i}{dT}$ and $\frac{dr_i}{dx}$ should be small, and hence $\frac{d\mathcal{E}}{dT}$ and $\frac{d\mathcal{E}}{dx}$ should be small, if $\frac{d \ln a_i}{dT}$ and $\frac{d \ln a_i}{dx}$ are small. For many molten salt mixtures investigated in the present work it is true that $\frac{d\mathcal{E}}{dT}$ is very small, particularly for mixtures rich in lead halide.

(iv) Calculation of Diffusion Potentials

We wish to examine the possibility of theoretical calculation of diffusion potentials on the basis of specific models for the molten electrolyte, in order to assess - by comparison of the calculated with the observed values of $\mathcal{E}$ - the validity of particular structural models.

Let us consider first the general equation for the diffusion potential

$$\mathcal{E} = -\frac{RT''}{F'}\int \sum_n \frac{t_i}{z_i}\, d \ln a_i \qquad \text{(equation (53))}$$

It is not possible to calculate $\mathcal{E}$ directly from this equation; the equation must be integrated and the integration requires the use of certain assumptions. In the first place, there is at present no way of assignment of values to the ionic activities a_i and hence we make the basic approximation

$$f_i = 1, \quad \text{for all } i.$$

As pointed out in the previous section, this is not the least restrictive assumption which may be made, but it will suffice for the present purpose. The second assumption required concerns the nature of the liquid junction - the Henderson assumption (the "continuous - mixture" boundary) is probably a good approximation for the cells studied in the present work. In the Henderson integration of the fundamental equation, a third assumption is made, namely that the mobility of any ionic species is the same on both sides of the liquid junction. There is at present insufficient experimental data available to test this assumption. The final step in the calculation of diffusion potentials is the adoption of a specific structural

model. It will become apparent that for all except relatively simple models, the calculation is extremely difficult.

We utilise, for the calculation, the Henderson equation, because it is probable that this is the most applicable of the known integrated forms of the fundamental equation. Let us consider the simplest model, i.e. that the electrolyte PbX_2 - MX is completely dissociated into the simple ions Pb^{2+} , M^+ and X^- . Then the expression for the diffusion potential becomes, on simplification

$$\xi \pm \frac{RT}{F}\left(\frac{\frac{1}{2}u_{Pb^{2+}} - u_{M^+} - u_{X^-}}{u_{Pb^{2+}} - u_{M+} + u_{X-}}\right) \ln\left(\frac{u_{Pb^{2+}} + 2u_{X^-}}{x\left(u_{Pb^{2+}} - u_{M+} + u_{X-}\right) + u_{M+} + u_{X^-}}\right) \quad \ldots(69)$$

We require now values for $u_{Pb^{2+}}$, u_{M+} and u_{X^-}. In the absence of experimental values, there appears to be no unique way of assigning numerical values to the u_i . They are related to the equivalent conductance of the electrolyte but in order to calculate the u_i from Λ mixt. it is necessary to make further assumptions concerning their relative magnitudes. For the purpose of calculating approximate values for the ionic mobilities we make, as a first approximation, the following assumptions:

(a) In the molten electrolyte the ions migrate independently.

(b) The parameters $u_{Pb^{2+}}$, u_{M+} and u_{X^-} are invariant with respect to the composition of the electrolyte PbX_2 - MX; we make the crude approximation that the three ions have the same mobilities in the molten mixture as in the pure salts PbX_2 and MX.

(c) Transport numbers of ions in molten salts are invariant with respect to temperature.

For the calculation of u_{M+} and u_{X-} in the pure molten alkali halides we require values for the transport numbers t_{M+} (or t_{X-}). It appears that the transport numbers only for the alkali chlorides have been measured and hence we shall be restricted to treatment of the systems $PbCl_2$ - MCl. We shall further restrict the treatment to one temperature, 720° C, because Λ mixt. is known only at this temperature, for the chloride systems.

The specific conductances for the alkali chlorides have been measured by Van Artsdalen and Yaffe[1]. From these data, in conjunction with the densities of the salts[1], we deduce for the equivalent conductances of the salts the values (in ohm^{-1} cm^2 equiv^{-1} units)

$$\Lambda_{LiCl} = 182.68,\ \Lambda_{NaCl} = 121.42,\ \Lambda_{KCl} = 96.21,\ \Lambda_{RbCl} = 80.69$$

$$\Lambda_{CsCl} = 82.89.$$

From the equation

$$\frac{\Lambda}{F}_{\text{mixt.}} = \left(\frac{2x}{1+x}\right) u_{Pb^{2+}} + \left(\frac{1-x}{1+x}\right) u_{M+} - u_{X-}$$

we obtain the relationships:

$$u_{Li^+} - u_{Cl^-} = 18.93 \times 10^{-4},\quad u_{Na^+} - u_{Cl^-} = 12.58 \times 10^{-4},$$

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1. Van Artsdalen and Yaffe, J. Physic.Chem., 59, 118 (1955)
2. Yaffe and Van Artsdalen, J.Physic.Chem., 60, 1125 (1956)

$u_{K^+} - u_{Cl^-} = 9.97 \times 10^{-4}$, $u_{Rb^+} - u_{Cl^-} = 8.36 \times 10^{-4}$,

$u_{Cs^+} - u_{Cl^-} = 8.59 \times 10^{-4}$.

The units of $(u_{M^+} - u_{X^-})$ are $cm^2\ volt^{-1}\ sec^{-1}$. We now make use of the transport number data:

LiCl (600°C), $t_{Li^+} = 0.75$ [1]; NaCl (860° C), $t_{Na^+} = 0.62$ [1];

KCl (830°C), $t_{K^+} = 0.62$ [1]; RbCl (785°C), $t_{Rb^+} = 0.58$ [1];

CsCl (685° C), $t_{Cs^+} = 0.565$ [1,2].

Assuming that the transport numbers have the same values at 720° C, we deduce for the mobilities of the ions (in $cm^2\ volt^{-1}\ sec^{-1}$ units):

for LiCl, $u_{Cl^-} = -4.74 \times 10^{-4}$, ($u_{Li^+} = 14.19 \times 10^{-4}$);

for NaCl, $u_{Cl^-} = -4.78 \times 10^{-4}$, $u_{Na^+} = 7.80 \times 10^{-4}$;

for KCl, $u_{Cl^-} = -3.79 \times 10^{-4}$, $u_{K^+} = 6.18 \times 10^{-4}$;

for RbCl, $u_{Cl^-} = -3.51 \times 10^{-4}$, $u_{Rb^+} = 4.85 \times 10^{-4}$;

for CsCl, $u_{Cl^-} = -3.74 \times 10^{-4}$, $u_{Cs^+} = 4.86 \times 10^{-4}$.

The mean of these values for u_{Cl^-} is -4.11×10^{-4}, and we take this value to be the value of u_{Cl^-} in $PbCl_2$ - MCl mixtures and in pure $PbCl_2$ at 720°C. We assume further that the above values of u_{M^+} are those appropriate to the salt mixtures at the same temperature.

To determine $u_{Pb^{2+}}$ we make use of the equation

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1. Duke and Bowman, J.Electrochem.Soc., 106, 622 (1959)
2. Wolf, J.Electrochem.Soc., 108, 811 (1961)

$$\frac{\Lambda_{PbCl_2}}{F} = u_{Pb^{2+}} - u_{X^-}$$

From the known values of κ_{PbCl_2} [1] and ρ_{PbCl_2} [2], it is possible to calculate $\frac{\Lambda_{PbCl_2}}{F}$; the result is

$$\frac{\Lambda_{PbCl_2}}{F} = 7.50 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$$

Hence we obtain

$$u_{Pb^{2+}} = 3.39 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$$

We may calculate a value for u_{Pb2+} from the transport number data presented in Chapter 2. Using the values

$$t_{Cl^-} = 0.37 \text{ , } t_{Pb2+} = 0.63$$

we find

$$u_{Pb2+} = -\frac{0.63}{0.37} \cdot u_{Cl^-} = 7.02 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$$

This value for $u_{Pb^{2+}}$ is in poor agreement with the value calculated from conductance data.

Substitution of the values for the u_i in equation (69) leads to the following results: Setting P equal to the prelogarithmic factor and Q equal to the logarithmic factor we find that, for

I $PbCl_2$ - CsCl; $P < 0$, hence $\varepsilon < 0$, for all x in the range x=1.00 to x=0.25;

II $PbCl_2$ - RbCl; $P < 0$, hence $\varepsilon < 0$, for all x in the range x=1.00 to x=0.25;

III $PbCl_2$ - KCl; $P > 0$, but $Q < 0$ over most of the composition range - if

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1. Harrap and Heymann, Trans. Faraday Soc., 51, 259, 268 (1955)
2. Boardman, Dorman and Heyman, J.Physic.Chem., 53, 375 (1949)

$Q < 0$ then $\mathcal{E}$ is indeterminate;

IV $PbCl_2$ - NaCl; $P > 0$, but $Q < 0$ over most of the composition range.

It is apparent that the approach is invalid.

A somewhat similar approach may be made on the basis of the Stokes Law equation

$$| u_i | = 1 / 6 \pi \eta r_i \qquad \ldots(70)$$

in which η is the viscosity of the medium, r_i is the radius of species i. The applicability of this equation has not been fully demonstrated for molten salt systems but there is evidence that it should be at least a reasonably good approximation. From equation (70) we may state that for a mixture of given composition, the product ($| u_i |$ r_i) should be constant. Hence we may substitute for the u_i in equation (69) by use of the relationship

$$| u_i | = \frac{k}{r_i} \qquad \ldots(71)$$

where k is the proportionality constant and has the value given by

$$k = (1 / 6 \pi \eta).$$

Combination of (69) and (71) yields

$$\mathcal{E} = \frac{RT}{F} \left(\frac{\frac{1}{2r_{Pb^{2+}}} - \frac{1}{r_{M+}} + \frac{1}{r_{X^-}}}{\frac{1}{r_{Pb^{2+}}} - \frac{1}{r_{M^+}} - \frac{1}{r_{X^-}}} \right) \ln \frac{\frac{1}{r_{Pb^{2+}}} - \frac{2}{r_{X^-}}}{X\left(\frac{1}{r_{Pb^{2+}}} - \frac{1}{r_{M+}} - \frac{1}{r_{M+}} \right) - \frac{1}{r_{X^-}} + \frac{1}{r_{M^+}}} \qquad \ldots(72)$$

Substituting accepted values[1] for the radii of Pb^{2+}, Cl^- and alkali metal ions, it follows that for :

I $PbCl_2$ - CsCl; $P < 0$, hence $\varepsilon < 0$, for all x in the range x=1.00 to x= 0.25;

II $PbCl_2$ - RbCl; $P < 0$, hence $\varepsilon < 0$, for all x in the range x=1.00 to x=0.25;

III $PbCl_2$ - KCl; $P < 0$, hence $\varepsilon < 0$, for all x in the range x=1.00 to x=0.25;

IV $PbCl_2$ - NaCl; $P > 0$, but $Q > 0$ for most values of x, i.e. ε is indeterminate for all compositions except those close to the pure lead chloride composition.

Thus, this approach leads to values of ε widely different from experimental values for cases I, II and III, and incalculable values of ε in case IV. There are however theoretical reasons for this result and also the result obtained with the first approach (above). From equation (63), we have the conditions for $\varepsilon \neq 0$:

$$\text{for } \varepsilon > 0, \; u_1 < u_2$$

$$\text{for } \varepsilon < 0, \; u_1 > u_2 \qquad \ldots(73)$$

Application to (73) of the Stoke's Law relationship, $|u_i| = K / r_i$, yields the conditions:

$$\text{for } \varepsilon > 0, \; r_i > r_2$$

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1. Pauling, "Nature of the Chemical Bond," Cornell University Press, New York (1948)

for $\mathcal{E} < 0$, $r_1 < r_2$ ...(74b)

Condition (74a) is satisfied by the ions Cs^+, Rb^+ and K^+; hence for the systems $PbCl_2$ - CsCl, $PbCl_2$ - RbCl and $PbCl_2$ - KCl $\mathcal{E}$ is necessarily negative (for all values of x) when calculated on the basis of Stoke's Law. The assumption was also made implicitly, in this treatment, that u_i (i denoting Pb^{2+}, M^+ or Cl^-) is composition invariant - this is a very crude approximation.

We consider now a third approach to the calculation of diffusion potentials - in essence merely a third method of assignment of numerical values to the ionic mobilities u_i. Let us assume that the alkali metal cation, M^+, has the same mobility as in pure molten MCl, and that its mobility is invariant with respect to the composition of the mixture. We allow u_{Pb2+} and u_{X^-} to cary with composition. Then we have,

$$\left(\frac{2x}{1+x}\right) u_{Pb^{2+}} - u_{X^-} \pm\left[\frac{\Lambda}{F}\text{ mixt.} - \left(\frac{1-x}{1+x}\right) u_{M+}\right] \quad ...(75)$$

The term on the right hand side of equation (75) has known value, Λ mixt. being derived from the data of Bloom and Mackey[1]. In order to deduce the values of u_{Pb2+} and u_{X^-} we must make a further assumption, concerning their relative magnitudes. Let us assume in the first instance that the ratio ($u_{Pb^{2+}} / u_{Cl^-}$) has the same value in the molten mixtures as in pure molten $PbCl_2$. Then

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1. Bloom and Mackey, to be published (Trans. Faraday Soc.)

$$\frac{u_{Pb^{2+}}}{u_{Cl^-}} = - 0.825 \qquad \ldots(76)$$

and by combining (130) and (131) we may calculate $u_{Pb^{2+}}$ and u_{X^-}, and thus ε, at each composition.

These computations have been performed for mixtures corresponding to x_{PbCl_2} ranging from 0.95 to 0.25, for each of the four systems $PbCl_2$ - CsCl, $PbCl_2$ - RbCl, $PbCl_2$ - KCl and $PbCl_2$ - NaCl. The results are shown in Figures 24, (i) to (iv), along with experimental data of Richards [1] for the systems $PbCl_2$ - KCl and $PbCl_2$ - NaCl, and the experimental data obtained by the present author for the systems $PbCl_2$ - CsCl and $PbCl_2$ - RbCl. It is apparent, from Figures 24, that the calculated values of ε are in reasonably good agreement (with regard to both sign and magnitude) with the observed values, for mixtures rich in $PbCl_2$, indicating that the assumed model is at least feasible for such mixtures. As the proportion of alkali halide in the mixture increases, the calculated values of ε become much too high - they rapidly tend towards infinity - and the model is obviously quite inappropriate in these regions of composition.

It is possible to repeat the calculations outlined above, using different values for the ratio ($u_{Pb^{2+}} / u_{Cl^-}$). While such procedures would change the magnitude of ε (calculated), they would not significantly alter the shapes of the curves. In practice, of course, the ratio ($u_{Pb^{2+}} / u_{Cl^-}$) would almost certainly vary with electrolyte composition, but it is not

1. Bloom and Richards, to be published; Richards, Ph.D.Thesis, University of New Zealand (1956)

possible at present to make any less arbitrary assumption concerning the magnitude of this ratio. A rather more critical factor is the variation of u_{M+} with composition. The assumption that u_{M+} is invariant with respect to composition is obviously unreal, but again it does not appear possible to make any less arbitrary assumption concerning the dependence of u_{M+} on composition.

The treatment above illustrates the fact that the calculation of diffusion potentials(and hence quantitative testing of structural models) involves in essence assignment of numerical values to ionic mobilities - this is the most difficult part of the calculation. For more complex models than that considered, there is no obvious method of carrying out the assignments necessary.

FIGURE 24

Comparison of calculated and measured values of the diffusion potential.

FIGURE 24 (1)

System $PbCl_2$ - CsCl. Curve (a) shows the calculated 720°C isotherm; curve (b) shows the experimental 700°C isotherm (from data obtained in the present work.)

FIGURE 24(i)

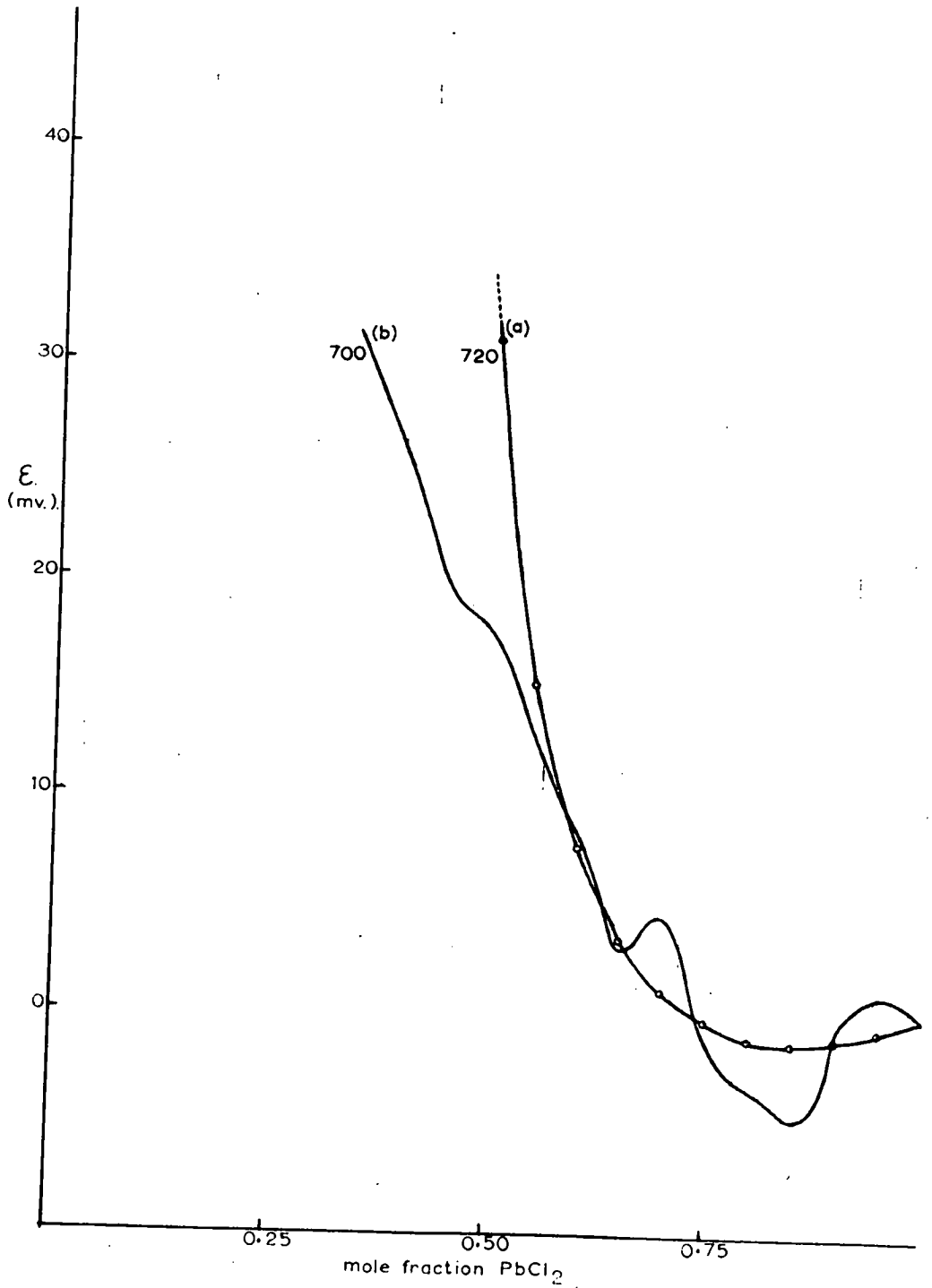


FIGURE 24 (ii)

System $PbCl_2$ - RbCl. Curve (a) shows the calculated 720°C isotherm; curve (b) shows the experimental 700°C isotherm (from experimental data obtained in the present work.)

FIGURE 24(ii)

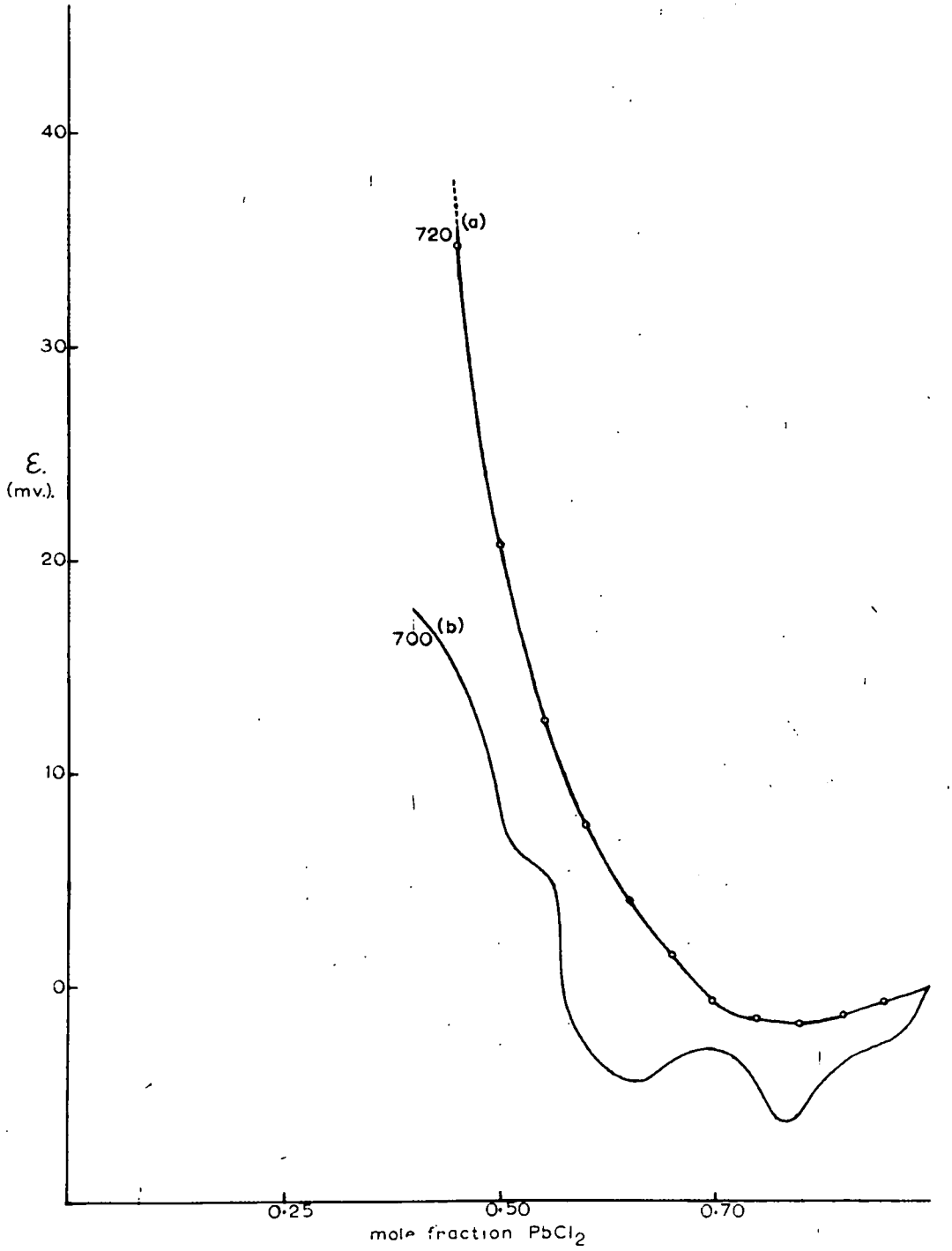


FIGURE 24 (iii)

System $PbCl_2$ - KCl. Curve (a) shows the calculated 720°C isotherm; curves (b) and (c) show the experimental 650°C and 750°C isotherms respectively, from data obtained by Richards[1].

(1) Bloom and Richards, to be published; Richards, Ph.D .Thesis, University of New Zealand (1956).

FIGURE 24(iii)

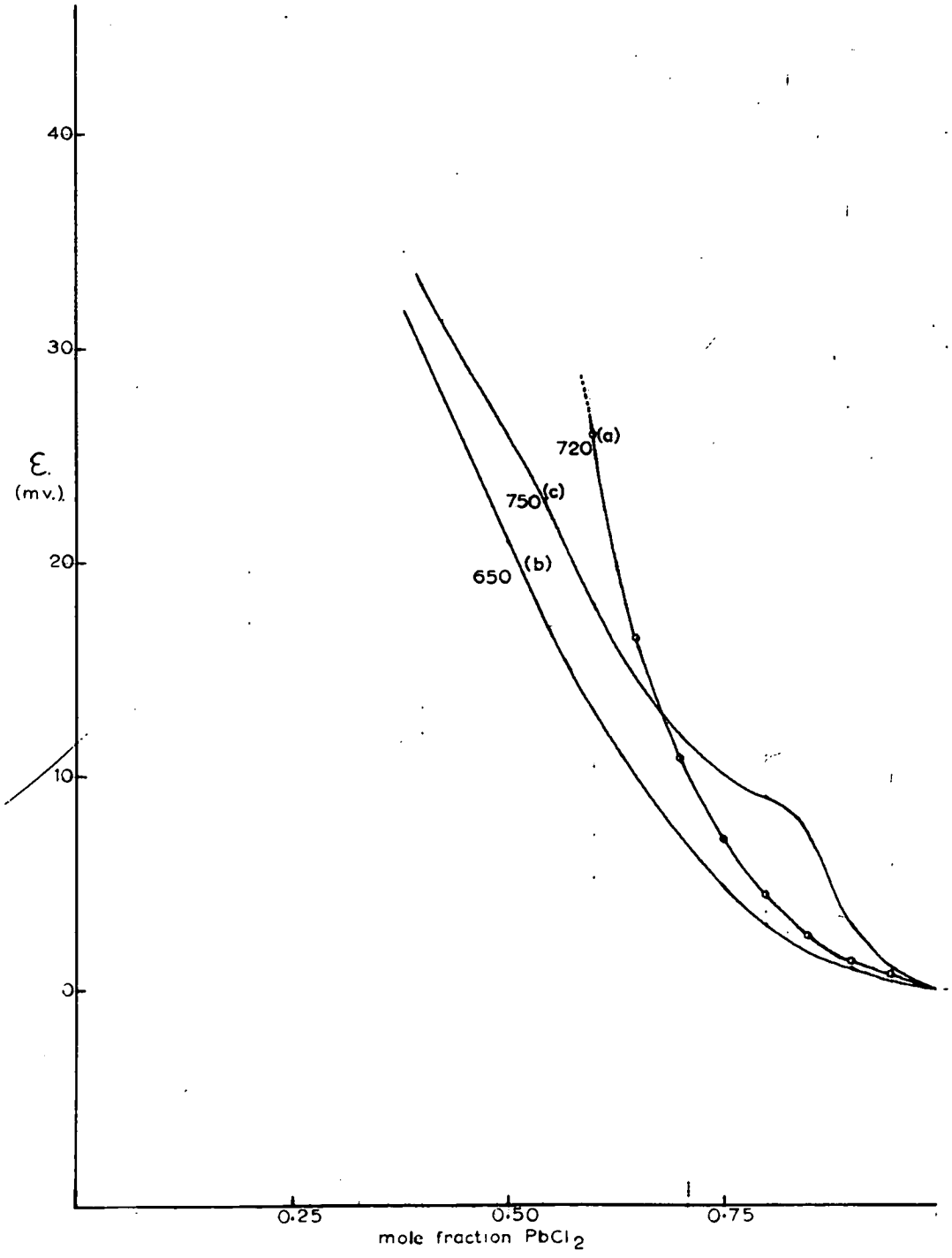
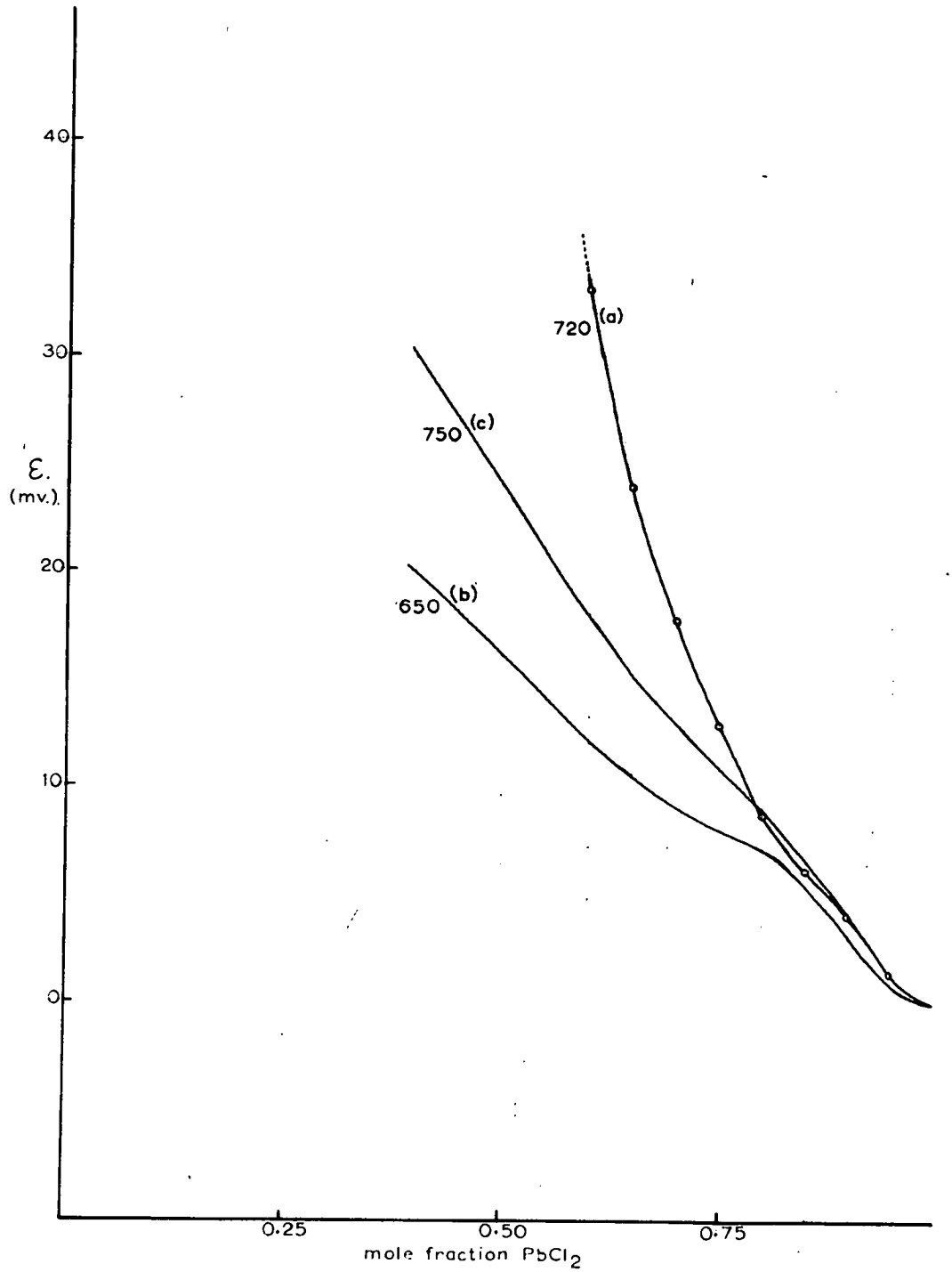


Figure 24 (iv)

System $PbCl_2$ - NaCl. Curve (a) shows the calculated 720°C isotherm; curves (b) and (c) show the experimental 650°C and 750°C isotherms respectively, from the data of Richards[1].

1. Bloom and Richards, to be published; Richards, Ph.D.Thesis, University of New Zealand (1956)

FIGURE 24(iv)


40
30
20
10
0
E.
(mv.)
720
(a)
750
(c)
650
(b)
0.25
0.50
0.75
mole fraction PbCl2

5. The Calculation of Thermodynamic Activities from the E.M.F's of Concentration Cells with Transference

Consider the cell with transference represented by

$$\underset{\text{electrolyte 1}}{Pb \mid PbX_2} \;\vdots\; \underset{\text{electrolyte 11}}{PbX_2 + MX \mid Pb}$$

If the E.M.F. of this cell is E_t and the E.M.F. of the corresponding cell without transference is E, then

$$E = -\frac{RT}{2F} \ln \frac{a_{II}}{a_{I}} \qquad \ldots(77)$$

and

$$E_t = E + \varepsilon \qquad \ldots(78)$$

where a_I and a_{II} are the activities of PbX_2 in the two electrolytes I and II. In case that $\varepsilon = 0$, then $E_t = E$. In the cell considered above $a_I = 1$ by definition (lead halide in its standard state). Hence it follows from (77) and (78) that if the diffusion potential vanishes then

$$E_t = -\frac{RT}{2F} \ln a_{II} \qquad \ldots(79)$$

and the activity a_{II} of lead halide in the molten mixture may be calculated from measured values of the E.M.F. E_t.

This is a valid measurement of activity if and only if the diffusion potential vanishes. Evidently workers [1] have assumed the diffusion potential to be zero, in particular cases, for the purpose of calculating activities in this way (i.e. from equation (79)). It has, furthermore, been assumed that if ε is small (of the order 1 - 2 millivolts

1. Inter alia, Murgulescu and Sternberg, Disc.Faraday Soc., 32, 107 (1961)

say) then no sensible error is introduced into the activity values by its neglect. Reference to Figures 25 and 26 indicates that such is not the case, at least for systems of the type PbX_2 - MX (where M ≡ Na, K, Rb, Cs; X ≡ Cl, Br). It appears that even for mixtures of composition close tothe pure lead halide composition $\mathcal{E}$ is in general about 20% of the E.M.F., E, of the cell without transference : in some cases, e.g. for the system $PbBr_2$ - KBr, $\mathcal{E}$ is of the same order as E. Thus, for small values of $\mathcal{E}$, ofthe order 1 - 2 millivolts, $\mathcal{E}$ / E has a relatively large value and hence the neglect of the contribution to E_t from the diffusion potential would introduce serious error into activities calculated on the basis of equation (79).

FIGURE 25

Plot of the ratio of diffusion potential (absolute value) to E.M.F of cell without transference (E), against E : systems $PbBr_2$ - CsBr, $PbBr_2$ - RbBr, $PbBr_2$ - KBr and $PbBr_2$ - NaBr.

FIGURE 25

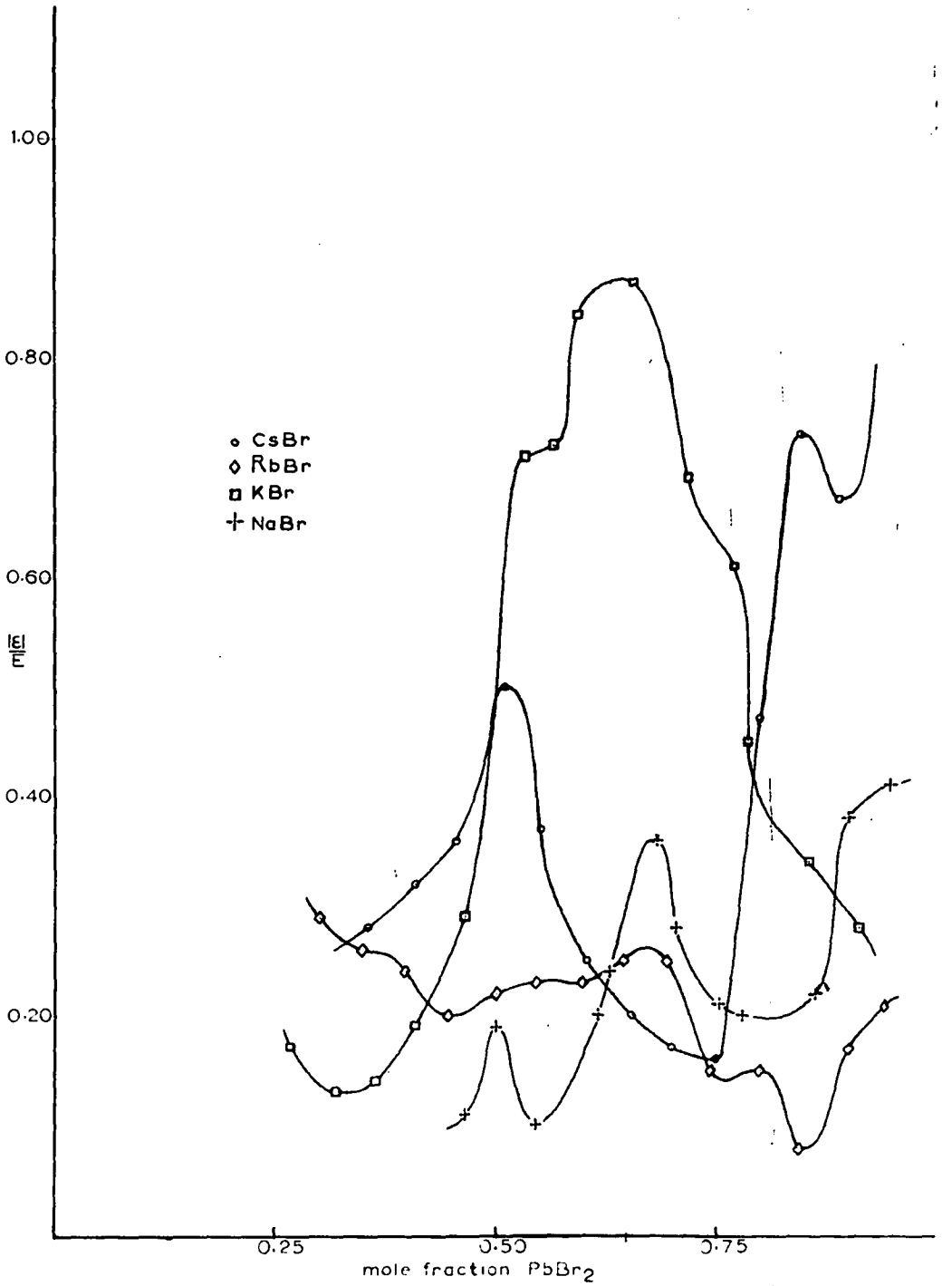
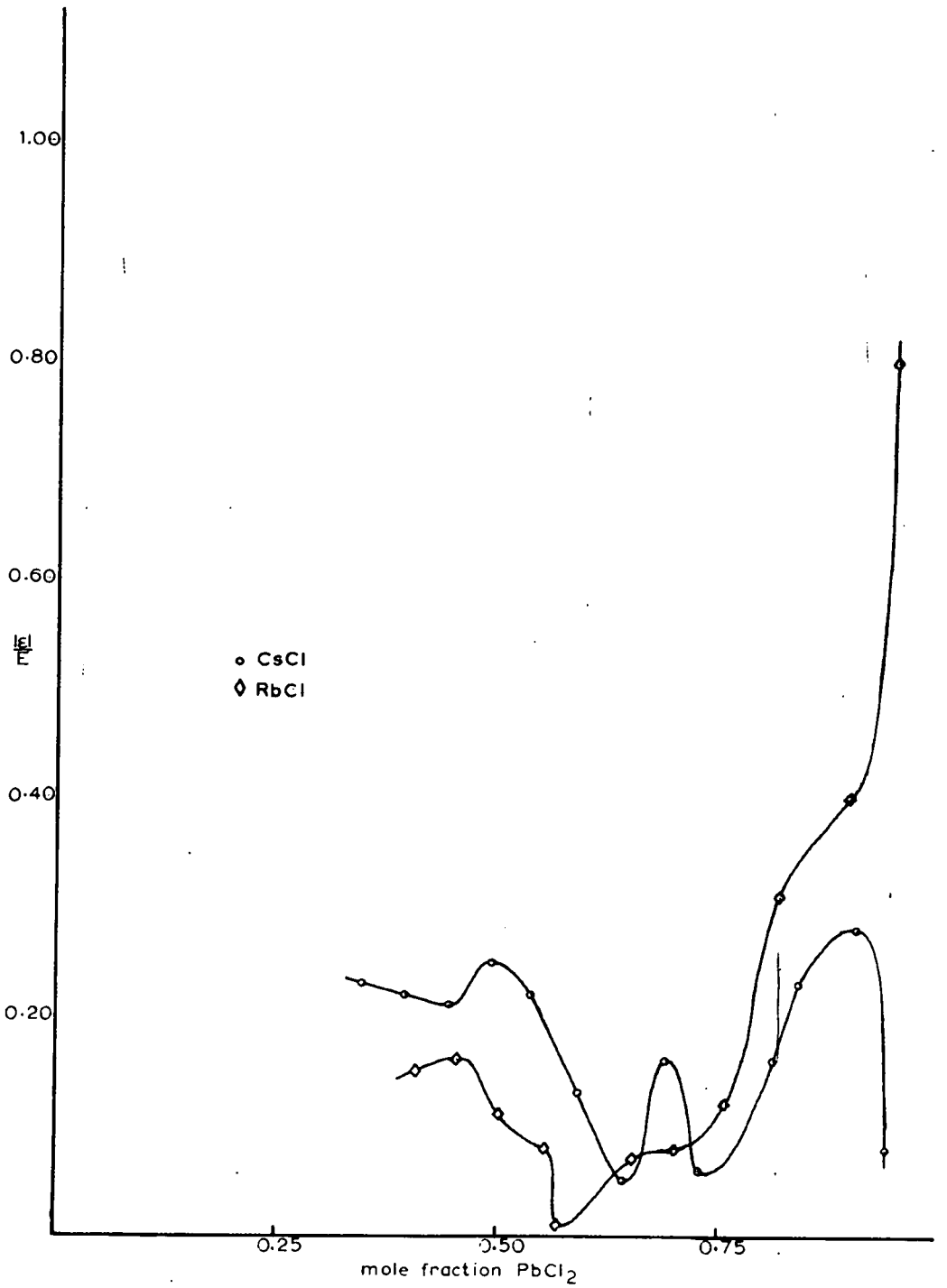

1.00
0.80
0.60
0.40
0.20
|ε|/E
CsBr
RbBr
KBr
NaBr
0.25
0.50
0.75
mole fraction PbBr2

FIGURE 26

Plot of the ratio of diffusion potential (absolute value) to E.M.F of cell without transference (E), against E : systems $PbCl_2$ - CsCl and $PbCl_2$ - RbCl.

FIGURE 26


1.00
0.80
0.60
0.40
0.20
|ε|/E
o CsCl
◊ RbCl
0.25
0.50
0.75
mole fraction PbCl2

APPENDIX 1.

"Least - squares" Computations

The computer programme which was utilised for the "Least - squares" computations of lines of best fit, is reproduced in Figure A (1) below. The programming language is the modification of Algol 60 known as Elliot 503 Algol. The computations were carried out at the Computer Centre of the University of Tasmania.

FIGURE A 1.

Computer programme used for the "least-squares" computation of lines of best fit.

FIGURE A1

```
Method of least squares;

begin integer L,SetNo,j,n;
        real p,q,r,s,A,B,P,Q;
        switch S:=L1;

        boolean procedure ng(i); value i; integer i;
        begin switch s:=1;
              elliott(0,2,0,0,0,0,0);
              elliott(0,0,1,1,5,4,8191);
              elliott(1,6,1,0,7,0,0);
              elliott(2,3,1,0,4,3,1);
          1:  ng:=i ≠ 0
        end ng(i);


procedure page;  comment requires global variable L;
        begin switch ss:=s1;
           s1:if L=0 then print £Set No£t?a£t?b?;
              if L=55 then      begin print ££1117?;
                                      L:=0;
                                      goto s1
                                end;
              L:=L+1
        end page;

        L:=0;
        sameline;digits(3);
    L1: read SetNo,n;
        begin array a,b[1:n];
                  page;
                  p:=0;
                  q:=0;
                  for j:=1 step 1 until n do
                  begin read a[j],b[j];
                            p:=p+a[j];
                            q:=q+b[j]
                  end;
                  r:=p/n;
                  s:=q/n;
                  A:=0;
                  B:=0;
                  for j:=1 step 1 until n do
                  begin       P:=a[j]-r;
                              Q:=b[j]-s;
                              A:=A+P*Q;
                              B:=B+P*P
                  end;
                  print ££1s2??,SetNo,££s3??,aligned(3,3),s-A/B*r,££s4??,aligned(1,4),A/B;

                  if ng(1) then begin if ng(2) then wait;
                                      goto L1
                                end
        end
end;
```

APPENDIX 2

Preparation of lead halide - alkali halide complex compounds, from aqueous solution

Attempts have been made by the author to recover rubidium and caesium chlorides from $PbCl_2$ - RbCl and $PbCl_2$ - CsCl solid mixtures. The procedure used consisted in extraction of the finely ground mixtures by shaking with water, filtration to remove the undissolved solid (mainly $PbCl_2$) and concentration of the filtrate. On cooling the concentrated filtrate a further quantity of $PbCl_2$ crystallised out. In general after this concentration / crystallisation procedure had been repeated two or three times, the solid crystallising out from solution was found not to be pure $PbCl_2$ but rather, complex compounds of the general type Mx Pby X_{x+2y} . In one case a cold filtrate (containing dissolved $PbCl_2$ and RbCl) was allowed to stand, to slowly evaporate the water solvent, for a period of several months. By the end of this period large, apparently orthorhombic crystals had appeared. The crystals possessed the unusual property of extreme adherence to glass, and appeared from microscopic examination to be entirely homogeneous, i.e. consisting of a single pure compound. By analysis for lead, chlorine and rubidium the formula of the compound was found to be Rb Pb_4 Cl_9 , and the structure has been established by Finney[1], using X-ray diffraction techniques.

---

1. Finney, Thesis, University of Tasmania (1964)

This compound appears not to have been previously prepared. The author has attempted to repeat the preparation, but to date all attempts have been unsuccessful. Evidently for this preparation the relative concentrations of RbCl and $PbCl_2$ are critical.

Other compounds have been prepared in a similar manner; they include Pb Pb_2 Cl_5 , Cs Pb Cl_3 , Cs_2 $PbCl_4$ and Cs Pb_2 Cl_5 - all these compounds have been prepared previously.

In another attempted extraction of RbCl - $PbCl_2$ mixtures, waste liquors from analyses were used. The waste liquors were solutions dilute with respect to $PbCl_2$, RbCl and CH_3 COOH, and concentrated with respect to NH_4OO CH_3 . The solutions (of various relative concentrations of the solutes) were combined and evaporated to small volume. The cold concentrated solution was then allowed to stand. After a period of four to five months large rhomb-shaped crystals appeared, and on analysis the compound was found to have the formula Rb Pb_3 Cl_7 . This compound appears not to have been previously prepared. Again, attempts to repeat the preparation have failed, to date. The structure of the compound has not yet been determined.

ACKNOWLEDGEMENTS

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